CANADIAN JOURNAL
OF SOIL SCIENCE

VOLUME 38 AUGUST 1958 No. 2

# THE LIMING OF DIKELAND SOILS[1]

L. B. MacLeod[2]

*Canada Department of Agriculture, Nappan, Nova Scotia*

[Received for publication September 17, 1957]

## ABSTRACT

In a greenhouse study dolomitic and calcitic limestone were applied at rates of 0, 2, 4, 6 and 8 tons per acre to three samples of dikeland soil representative of surface soil, sub-soil and a mixture of the two. The two kinds of limestone were equally effective in increasing crop yields and there were no significant yield differences with different soils, when limed at the appropriate rate. Increases in yield due to liming were highly significant, but significance of the yield increases for successive increases in rate of liming varied with different crops. The increases in grain and clover yields above the 6-ton rate were, on the average, small and not significant.

Where dolomitic limestone was applied the Ca:Mg ratio remained approximately 1 : 1 in all soils. The application of calcitic limestone resulted in a Ca:Mg ratio ranging from 2 : 1 for the 2-ton rate to 5 : 1 for the 8-ton rate, but this wide range did not have any apparent effect on crop yield in this experiment.

## INTRODUCTION

Dikeland soils occupy some 80,000 acres and constitute an important part of the agricultural land in Nova Scotia and New Brunswick. These soils have been deposited over the centuries by the tides of the Bay of Fundy. Parent material was eroded from the neighbouring uplands, ground in the bay and then deposited by the receding tides on the bordering lowlands. Thus formed, they are level, deep and very fertile and when protected from the sea by dikes are capable of producing abundant crops (7). For maximum productivity, however, these soils must be adequately drained and their strongly acid reaction reduced by liming.

Dikeland flats at the Experimental Farm, Nappan, Nova Scotia, have, over a period of 30 years, shown marked increases in crop yields due to liming (1). Records indicate that liming rates of only 1.5 and 2.5 tons per acre every 6 years increased grain and hay yields by 65 and 35 per cent, respectively. Similar experiments have shown that phosphorus fertilization produced further increases while potassium fertilization did not noticeably affect crop yields (1). The primary requirement of these soils when adequately drained, however, is the application of lime to correct their acid condition.

[1] Presented before the Canadian Society of Soil Science, Vancouver, B.C., June 25, 1957. Contribution from Field Husbandry Division, Experimental Farms Service.

[2] Agronomist, Soil Fertility, Canada Department of Agriculture, Nappan, N.S.

Unlimed dikeland soils have a relatively high magnesium content (1) and it has been suggested that when liming it would be preferable to use a high-calcium or calcitic liming material, rather than one containing a large proportion of magnesium. Because of the limited amount of information available in this respect, a greenhouse experiment was designed to study the relative merits of calcitic and dolomitic limestones at relatively high rates of application. Since certain dikeland drainage practices involve grading and the consequent exposure of the sub-soil, a study on the reaction of top-soil, sub-soil and a mixture of the two to liming was included in the experiment. The results are presented in this paper.

## EXPERIMENTAL MATERIALS AND METHODS

Samples of soil were obtained from dikeland flats on the property of Radio Station CBA near Sackville, New Brunswick. These flats are under experiment and the conventional drainage method of a deep, narrow dale ditch which provides adequate drainage, but has certain disadvantages, is being compared with experimental drainage methods involving the grading of flats from the sides to the centre to form a V-shaped ditch and flats with raised crowns. As a result of the grading, sub-soil was exposed in some parts of each flat, while in other parts there was a mixture of sub-soil and top-soil. The soils used in the present study were as follows:

Soil No. 1—Surface soil from undisturbed flats—a dark brown, high organic matter soil representative of the 0—8-inch depth

Soil No. 2—Soil from the crowns of graded flats consisting of a mixture of surface soil and so-called sub-soil in approximately equal amounts

Soil No. 3—Soil from the sides of graded flats where the surface soil had been removed. This was a very heavy blue-grey, poorly-drained, putty-like soil which had not been weathered because of its waterlogged condition and which is referred to in this paper as sub-soil.

Dikeland soils are classified in soil survey reports (6) as the Acadia Association and the results of physical and chemical analysis of soil from several dikeland areas are discussed in a previous report (1).

TABLE 1.—CHEMICAL ANALYSIS OF SAMPLES OF DIKELAND SOIL TAKEN BEFORE LIMING

| — | pH | Exchangeable bases | | | Base exchange capacity | Base saturation | Phosphorus (Bray) | Nitrogen (total) | Organic matter |
|---|---|---|---|---|---|---|---|---|---|
| | | Ca | Mg | K | | | | | |
| | | m.e./100 gm. | | | m.e./100 gm. | % | p.p.m. | % | % |
| Soil No. 1 top-soil | 4.6 | 5.33 | 6.56 | 1.07 | 21.76 | 59.56 | 9 | 0.42 | 10.0 |
| Soil No. 2 top-soil and sub-soil | 4.1 | 2.75 | 5.88 | 0.92 | 21.04 | 45.39 | 9 | 0.34 | 7.9 |
| Soil No. 3 sub-soil | 4.0 | 2.30 | 4.96 | 0.95 | 20.60 | 39.85 | 11 | 0.29 | 6.1 |

Each of the samples was air-dried sufficiently to enable screening through a sieve with 1/3-inch mesh. After screening, each was mixed and placed in glazed gallon pots, 9 lb. per pot. Composite samples taken from each of the three soils before potting were air-dried and passed through a 2-mm. sieve. The chemical analyses of these samples are shown in Table 1.

Soil pH values were determined with a glass electrode, using a 1:1 soil-water ratio and base exchange capacity by distillation of adsorbed ammonia after treatment with ammonium acetate and leaching with sodium chloride as described by Peech *et al.* (4). Procedures given in "*Chemical Methods of Soil Analysis*" (8) were followed in the determination of exchangeable calcium, magnesium and potassium, total nitrogen by the Kjeldahl method, and organic matter by wet oxidation. The base saturation was obtained by expressing the sum of exchangeable bases as a per cent of the soil exchange capacity. Easily acid-soluble plus adsorbed phosphorus was determined using the procedure described by Bray (3).

Soil No. 1 was strongly acid in reaction, while soils No. 2 and No. 3 were both very strongly acid. Exchangeable potassium and easily acid-soluble plus adsorbed phosphorus were relatively uniform for all three soils. Organic matter and nitrogen contents were higher for Soil No. 1 than for Soils No. 2 and No. 3. The content of exchangeable calcium and magnesium decreased with depth of soil but that of exchangeable calcium was more pronounced.

The experiment was designed as a double-split plot to accommodate the three soils and two kinds of limestone in one experiment. Dolomitic and calcitic limestone were applied at the rate of 0, 2,000, 4,000, 6,000 and 8,000 p.p.m. or the equivalent of 0, 2, 4, 6, and 8 tons per acre. The calcitic limestone contained approximately 96 per cent calcium carbonate, while the dolomitic limestone contained 45 per cent calcium carbonate and 54 per cent magnesium carbonate. The limestone was thoroughly mixed with the contents of each pot receiving that treatment. The pots were watered and allowed to stand for a month, after which ammonium nitrate at the rate of 16 lb. N per acre, 20 per cent superphosphate at the rate of 75 lb. P per acre, and muriate of potash at the rate of 36 lb. K per acre were applied to each pot. Fertilizer was placed in the soil at a depth of 2 inches.

Scotian oats were seeded at a depth of 1 inch and double-cut red clover at a depth of one-half inch. The oats were later thinned to 8 plants and the clover to 12 plants per pot. The oats were harvested in the early spring and the clover crops in late spring and early summer as they reached the full-bloom stage. Yield data were recorded as dry matter in grams per pot.

Composite soil samples, consisting of one core from each of the four replications of any one limestone treatment were made after liming but before seeding, and again after the oats and two clover crops were harvested. These were air-dried and passed through a 2-mm. screen.

After the second sampling, the top 6 inches in the pots were inverted to simulate ploughing and left until early fall when a second crop of oats was seeded and harvested in the same manner as the first crop.

TABLE 2.—GREENHOUSE YIELDS OF CROPS GROWN ON DIKELAND SOIL (AVERAGE OF FOUR REPLICATES)

| Treatment | Soil No. 1 | | | | Soil No. 2 | | | | Soil No. 3 | | | | Mean of three soils | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Gr | St | Cl | Gr (2) | Gr | St | Cl | Gr (2) | Gr | St | Cl | Gr (2) | Gr | St | Cl | Gr (2) |
| | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. | gm. |
| Dolomitic lime: | | | | | | | | | | | | | | | | |
| 0 tons/acre | 6.0 | 14.5 | 27.2 | 3.9 | 6.0 | 11.0 | 3.0 | 3.1 | 5.3 | 11.0 | 1.8 | 2.0 | 5.7 | 12.2 | 10.7 | 3.0 |
| 2 tons/acre | 6.4 | 17.1 | 41.2 | 4.5 | 6.6 | 16.7 | 42.2 | 3.7 | 6.6 | 14.9 | 45.0 | 3.7 | 6.5 | 16.2 | 42.8 | 4.0 |
| 4 tons/acre | 6.9 | 17.6 | 46.8 | 4.6 | 8.0 | 18.8 | 44.7 | 4.8 | 8.1 | 19.4 | 51.5 | 4.7 | 7.7 | 18.6 | 47.7 | 4.7 |
| 6 tons/acre | 8.2 | 21.0 | 46.8 | 5.0 | 6.8 | 19.2 | 45.2 | 4.8 | 5.8 | 24.4 | 52.8 | 5.2 | 6.9 | 21.5 | 48.3 | 5.0 |
| 8 tons/acre | 7.1 | 21.6 | 46.2 | 4.7 | 6.7 | 22.5 | 47.7 | 4.4 | 8.1 | 23.6 | 57.5 | 4.6 | 7.3 | 22.6 | 50.5 | 4.6 |
| Mean of dolomitic | 6.9 | 18.5 | 41.6 | 4.4 | 6.8 | 17.6 | 36.6 | 4.2 | 6.8 | 18.6 | 41.7 | 4.0 | 6.8 | 18.2 | 40.0 | 4.3 |
| Calcitic lime: | | | | | | | | | | | | | | | | |
| 0 tons/acre | 5.9 | 17.4 | 11.7 | 3.3 | 5.9 | 12.6 | 2.2 | 2.4 | 5.2 | 11.5 | 3.0 | 2.3 | 5.7 | 13.8 | 5.6 | 2.7 |
| 2 tons/acre | 6.5 | 18.8 | 46.0 | 5.0 | 6.2 | 17.1 | 43.5 | 4.2 | 6.6 | 16.2 | 50.2 | 4.1 | 6.4 | 17.4 | 46.6 | 4.4 |
| 4 tons/acre | 6.6 | 21.9 | 45.2 | 5.3 | 6.6 | 22.6 | 47.5 | 4.5 | 7.1 | 22.4 | 47.5 | 4.4 | 6.8 | 22.3 | 46.7 | 4.7 |
| 6 tons/acre | 7.5 | 23.0 | 50.0 | 4.9 | 7.2 | 20.2 | 48.0 | 4.6 | 8.2 | 22.2 | 51.5 | 4.0 | 7.6 | 21.8 | 49.8 | 4.5 |
| 8 tons/acre | 7.4 | 25.9 | 48.5 | 5.1 | 6.0 | 23.2 | 48.2 | 5.1 | 9.4 | 22.6 | 52.2 | 4.4 | 7.6 | 23.9 | 49.6 | 4.9 |
| Mean of calcitic | 6.8 | 21.4 | 40.3 | 4.7 | 6.4 | 19.1 | 37.9 | 4.2 | 7.3 | 19.0 | 40.9 | 3.8 | 6.8 | 19.8 | 39.7 | 4.2 |
| Average for soils | 6.8 | 19.9 | 41.0 | 4.6 | 6.6 | 18.4 | 37.2 | 4.2 | 7.0 | 18.8 | 41.3 | 3.9 | 6.8 | 19.0 | 39.7 | 4.2 |

| L.S.D. for treatment means | Grain | Straw | Clover | Grain (2) |
|---|---|---|---|---|
| Between soils | | | | |
| 0.05 | 1.54 | 1.89 | 3.21 | 0.74 |
| 0.01 | 2.34 | 2.86 | 4.86 | 1.12 |
| Between kinds of lime | | | | |
| 0.05 | 0.66 | 1.10 | 2.44 | 0.67 |
| 0.01 | 0.94 | 1.58 | 3.51 | 0.97 |
| Between rates of lime | | | | |
| 0.05 | 0.76 | 1.46 | 3.46 | 0.55 |
| 0.01 | 1.00 | 1.93 | 4.59 | 0.73 |

## RESULTS AND DISCUSSION

*Yield of Oats and Clover*

The yields of grain (Gr), straw (St) and clover (Cl) for each treatment and the average values are given in Table 2, together with the appropriate L.S.D. values.

The results show that, under greenhouse conditions, there were highly significant increases in the yield of grain, straw and clover with the application of either dolomitic or calcitic limestone. On the average of all rates of application, the differences in yield of grain and clover crops due to kinds of lime were not significant. With straw, however, calcitic limestone showed a highly significant increase in yield over dolomitic limestone.

On the unlimed pots of the three soils differences in yield of grain were not significant, while the yield of clover on soil No.1 was significantly higher than on soils No. 2 and No. 3. When these soils were limed at the appropriate rate, however, they appeared capable of producing similar yields of oats and clover.

The yield increases for successive increases in rate of liming had varying significance for the different crops. For the first grain crop, significant increases in yield were shown for successive increases in rates between 0, 2 and 4 tons of dolomitic and between 0, 4 and 6 tons of calcitic limestone per acre. The greatest response to liming for grain was obtained on soil No. 3 which showed significant response to the 2-ton rate of both kinds of lime and highly significant response to higher rates with the exception of the 6-ton rate of dolomitic. It was observed that liming had effectively improved the physical condition and water-holding capacity of this soil which in the unlimed or original state had been unweathered and very poorly drained.

For the second grain crop, the 2-ton rate of dolomitic as well as calcitic limestone gave significant increases on all soils. On the average of all soils the increases in straw yield for successive increases in rate of liming were significant up to the 8-ton rate for dolomitic and for the 2-, 4- and 8-ton rates of calcitic limestone. For clover, the yield increases for successive increases in rate of application were significant at the 2-, 4- and 8-ton rates of dolomitic and at the 2-ton rate of calcitic limestone. Although there were some variations in the response to rates of lime on the individual soils, there were, on the average of all rates, no significant differences between grain and clover crops due to kinds of lime.

These results are in agreement with those of Reith (5) who worked on a comparison of calcitic and magnesian liming materials on upland soils. He found that liming produced very large increases in crop yields but that the difference between the yields produced by two types of material was insignificant.

*Analysis of Soil Samples*

The values for pH, exchangeable calcium and exchangeable magnesium for soil samples taken after one crop of oats and two crops of clover were grown are presented in Figures 1 and 2. Both types of liming materials produced similar increases in soil pH values. Calcitic limestone decreased

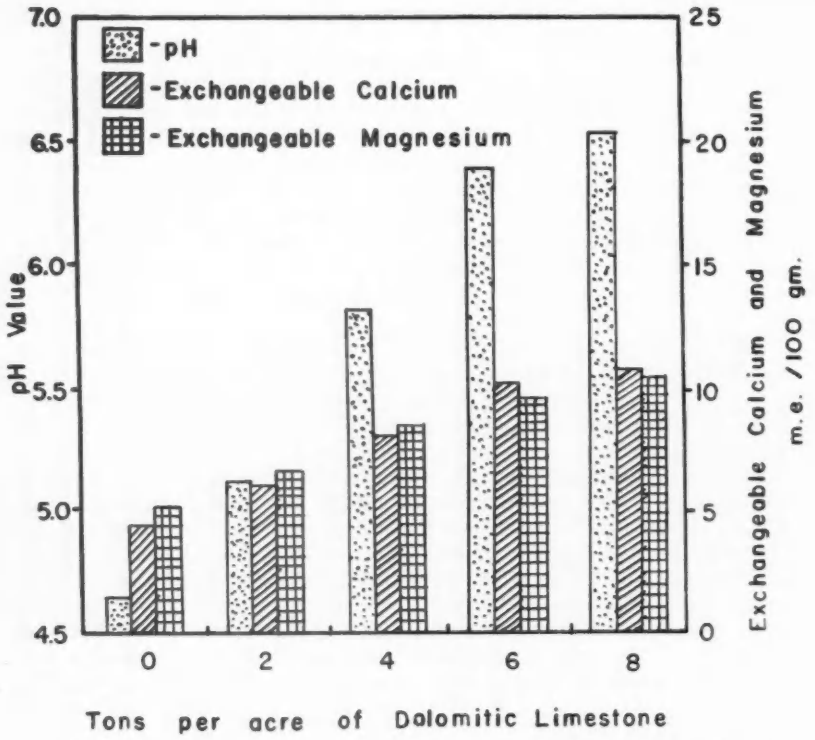



FIGURE 1. Diagram showing pH and exchangeable calcium and magnesium of dikeland soil that was limed at five rates with dolomitic limestone and cropped in the greenhouse.

soil acidity and increased exchangeable calcium, per cent base saturation and calcium : magnesium ratios. Where dolomitic limestone was applied soil acidity decreased, both exchangeable calcium and exchangeable magnesium increased and changes in the calcium : magnesium ratio were less marked than with the application of calcitic limestone.

Changes in base exchange capacity, total nitrogen, organic matter and Bray phosphorus due to liming and cropping were negligible with both liming materials. Where the 8-ton rate of limestone was applied, however, the per cent base saturation, as obtained by expressing the sum of the exchangeable bases as a per cent base exchange capacity, exceeded 100 per cent. These values probably resulted from free carbonates in the sample which, when brought into solution by ammonium acetate, gave high results for exchangeable calcium and magnesium.

The amounts of exchangeable calcium and magnesium are graphed in Figures 1 and 2 for the two kinds of limestone at all rates of application and represent the average of the three soils. Calcium : magnesium ratios were determined on a molar basis from these graphs using the values

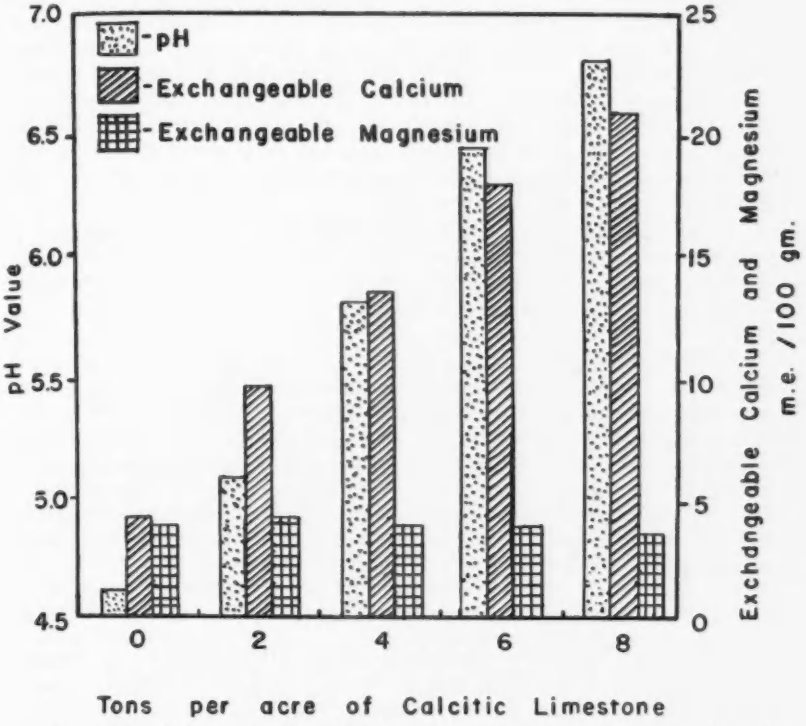



FIGURE 2. Diagram showing pH and exchangeable calcium and magnesium of dikeland soil that was limed at five rates with calcitic limestone and cropped in the greenhouse.

obtained by extraction with ammonium acetate solution under the conditions used. On dikeland soil, application of limestone had a definite effect on the Ca:Mg ratio and the different kinds of limestone reacted differently. Where dolomitic limestone was applied the Ca:Mg ratio remained approximately 1 : 1 for all soils, irrespective of rate of lime application. With calcitic limestone, however, the Ca:Mg ratio ranged from approximately 2 : 1 for the lowest to 5 : 1 for the highest rate of application. The wide range of Ca:Mg ratio resulting from liming with calcitic limestone did not have any apparent effect on crop yield in this experiment.

## CONCLUSIONS

The application of lime to dikeland soils resulted in highly significant increases in the yield of oats and clover under greenhouse conditions and similar results (1) were obtained in field trials* with oats and hay crops. Lime and phosphorus fertilizer were of major importance in developing the fertility potential of dikeland soils. On the average of all rates of

* *Unpublished data*, Experimental Farm, Nappan, N.S.

lime application there was no significant difference between dolomitic and calcitic limestone with regard to grain and clover yields. Straw yields, however, responded significantly to the higher rates of lime and calcitic limestone gave significantly higher yields than did dolomitic limestone. There were no apparent differences in element availability due to the kind of lime applied, and the wide range of Ca : Mg ratio, as determined in this experiment and resulting from liming with calcitic limestone, did not have any apparent effect on crop yield.

Significant differences in crop yield were obtained between successive increases in the rate of lime application, but this significance varied with different crops. On the average, however, grain and clover yields levelled off rapidly above the 6-ton rate and increases in yield above this rate were small.

All three soils responded equally well to liming and the application of lime at the appropriate rate was sufficient to equalize crop yields for the three soils under greenhouse conditions in this experiment. The results of this greenhouse trial show that the poorly-drained sub-soil, when exposed to weathering and adequately limed, was capable of producing crop yields comparable to those of the top-soil and suggest that, given adequate drainage, the application of higher rates of lime to the exposed sides of graded flats would tend to improve these areas and achieve a more uniform crop yield over the entire flat.

## ACKNOWLEDGEMENTS

The author wishes to acknowledge the contribution of R. F. Bishop, Officer-in-Charge, Chemistry Section, Science Service Laboratory, Kentville, Nova Scotia, and S. B. Williams, Superintendent, Experimental Farm, Nappan, Nova Scotia, for making suggestions and reviewing the manuscript, and the assistance of C. R. MacEachern, Assistant Chemist, who analysed the soil samples.

## REFERENCES

1. Baird, W. W. Report on dikeland reclamation, 1913 to 1952. Exptl. Farms Service Rept., Can. Dept. Agr. 1954.
2. Bear, F. E., and S. J. Toth. Influence of calcium on the availability of other soil cations. Soil Sci. 65:69-74. 1948.
3. Bray, R. H. Correlation of soil tests with crop response to added fertilizers and with fertilizer requirements. *In* Diagnostic techniques for soils and crops, pp. 58-86. Amer. Potash Inst., Washington, D.C. 1948.
4. Peech, M., *et al.* Methods of soil analysis for soil fertility investigations. Circ. 757, U.S. Dept. Agr. 1947.
5. Reith, J. W. S. Effects of calcitic and magnesian liming materials on the calcium and magnesium contents of crops and pasture. Empire J. Exptl. Agr. 22:305-13. 1954.
6. Whiteside, G. B., R. E. Wicklund, and G. R. Smith. Soil survey of Cumberland County, Nova Scotia. Rept. 2, Nova Scotia Soil Survey. 1945.
7. Williams, S. B. Maritime dikeland has excellent possibilities as pasture. *Research for Farmers*, Can. Dept. Agr. Quart. 1957.
8. Wright, L. E., *et al.* Chemical methods of soil analysis. Chemistry Div., Science Service, Can. Dept. Agr., Ottawa. 1949.

# PERSISTENCE OF BORAX IN SANDY SOILS[1]

G. J. OUELLETTE[2]

*Canada Department of Agriculture, Ste. Anne de la Pocatière, Quebec*

[Received for publication November 4, 1957]

## ABSTRACT

A field experiment was conducted on St. Pacôme sandy loam to study the movement and accumulation of applied boron within the soil profile, and consequently determine the optimum rate and frequency of borax application to the sandy soils of Eastern Quebec for the production of alfalfa hay and seed. From 65 to 75 per cent of the borax applied, depending upon the rate used, had moved below the 36-inch depth 30 months after application. The remaining portion was found, mostly in water-soluble form, below the 16-inch depth in the case of plots which had received borax at the 10- and 15-lb. rates, and in the entire profile, but with greater concentration in lower depths, in the case of plots which had received 25 and 40 lb. per acre. Very little fixation of the boron applied occurred between the surface and the 36-inch depth. The biennial application of 15 to 20 lb. of borax for alfalfa hay and 25 to 30 lb. for seed appeared satisfactory on that soil.

## INTRODUCTION

A survey conducted from 1950 to 1952 showed that approximately one-half of the alfalfa fields of Quebec required the addition of boron for the satisfactory production of alfalfa (8). Among the boron-deficient fields 70 per cent were on coarse-textured soils. In view of these results, it was believed advisable to determine the optimum rate and frequency of borax application to one of the coarse-textured soils for the production of alfalfa hay and seed. In this study, special attention was paid to the persistence or length of effectiveness of borax as related to its penetration.

In general, experiments to date indicate a very rapid downward movement of boron in sandy soils, necessitating frequent applications of borax (5, 7). Wilson, Lovvorn and Woodhouse (10) reported that, within 6 months, borax applications ranging from 10 to 40 lb. per acre were almost completely lost from the surface 8 inches of Norfolk sandy loam, while in Cecil clay very little had moved below the 8-inch depth. Field investigations conducted in New Zealand, British Columbia (11) and Connecticut (4) have shown that boron applied as borax moved to a depth of 30 inches in approximately 24 months. From leaching studies, Reeve, Prince and Bear (9) found that 75 to 85 per cent of a 20-lb. per acre application of borax was removed from 7-inch depths of four New Jersey soils, when water equivalent to one-fourth the annual rainfall of the region was applied.

## MATERIALS AND METHODS

Field plots were established on St. Pacôme sandy loam and seeded to alfalfa with oats as nurse crop in the spring of 1951. St. Pacôme sandy loam is a podzol soil, derived from gravelly and sandy marine terraces which are found at low elevations (50-250 feet) along the St. Lawrence River.

[1] Contribution from the Field Husbandry Division, Experimental Farms Service.
[2] Soil Fertility Specialist, Experimental Farm, Ste-Anne de la Pocatière, Que.

It is well drained, strongly acid, low in organic matter, and very low in over-all fertility. A brief description of a cultivated profile of St. Pacôme sandy loam follows:

| | | |
|---|---|---|
| Ac | 0-6 in. | Brown (10 YR 5/3; dark brown, 10 YR 4/3, moist) medium sand, weak granular structure, friable, pH 5.2 |
| $A_2$ | ----- | Remnants of the gray to pinkish gray leached sandy layer of the podzol still visible in the cultivated field |
| $B_{21}$ | 6-12 in. | Yellowish-brown (10 YR 5/6; dark brown, 10 YR 4/3, moist) medium sand, structureless or developed locally into an Ortstein, generally loose, pH 5.4 |
| $B_2C_1$ | 12-24 in. | Yellowish-brown (10 YR 5/4; very dark yellowish brown, 10 YR 4/4, moist) medium to coarse sand, friable and loose, with schistous gravel, pH 5.5 |
| $C_2$ | 24-30 in. | Yellowish-brown (10 YR 5/4; dark yellowish brown, 10 YR 4/4, moist) gravelly sand, loose, pH 5.6 |
| D | -30 in. | Light yellowish brown (10 YR 6/4; brownish yellow 6/6, moist) interstratified gravel and sand composed of sandstone, schist and quartzite, loose, pH 5.6. |

Calcitic limestone at the rate of 4 tons per acre was applied uniformly in the fall of 1951. Fertilizer was applied uniformly at the rate of 500 lb. 4-12-6 per acre at seeding time, and 0-20-20 at the rate of 500 lb. per acre in the fall every other year. The following rates of borax, applied once at seeding time or repeated every year from 1951 to 1954 inclusive, were used: 15, 25 and 40 lb. per acre. In addition, the 40-lb. rate was split in two 20-lb. applications made in 1951 and 1953, and also into four 10-lb. applications made every year from 1951 to 1954. The borax applied at seeding time was worked into the soil the day before seeding, whereas that applied on the sod in the following years was top-dressed in the early part of May. The borax used contained 44 per cent $B_2O_3$ or 13.6 per cent B. All borax treatments were replicated four times.

The randomized block design was used. The plot size was 20 by 20 feet. One-half of each plot, i.e. an area of 10 feet by 20 feet, was harvested twice a year as hay, and the other half only once a year for seed. These two cutting treatments were distributed at random within the plots. In 1951, oats was harvested at the early heading stage to encourage better growth of the alfalfa seedling.

Soil samples of the surface layer (0 to 8 inches) were collected each year in September. Ten cores were taken at random for each plot. In addition, samples of the following depth were taken in September 1956: 0 to 8 inches; 8 to 16; 16 to 24; 24 to 36. Water-soluble (available) boron in soil was determined by extraction with hot water and subsequent application of the quinalizarin colour reaction, in accordance with the method proposed by Berger and Truog (2). The fusion method also proposed by Berger and Truog was used to determine total boron in soil. Boron in plant tissue was determined by the quinalizarin method, following the ashing of a 0.50-gram sample of plant material in a muffle furnace at 450° C. for 8 hours.

TABLE 1.—YIELDS OF ALFALFA HAY AND SEED AS RELATED TO RATES AND FREQUENCY OF BORAX APPLICATION TO ST. PACÔME SANDY LOAM

| Treatment<br>Lb. of borax per acre | 1952 | | 1953 | | 1954 | | 1955 | | 1956 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Hay lb. D.M./a. | Seed lb./a. | Hay lb. D.M./a. | Seed lb./a. | Hay lb. D.M./a. | Seed lb./a. | Hay lb. D.M./a. | Seed lb./a. | Hay lb. D.M./a. | Seed lb./a. |
| Check | 2742 | 59 | 2247 | 41 | 3842 | 34 | 3767 | 51 | 2621 | 43 |
| 15 lb. in 1951 | 3447 | 113 | 2599 | 46 | 3627 | 41 | 3630 | 46 | 2741 | 31 |
| 25 lb. in 1951 | 3702 | 130 | 2639 | 65 | 4085 | 49 | 4081 | 57 | 2591 | 29 |
| 40 lb. in 1951 | 3842 | 138 | 3060 | 74 | 4004 | 44 | 4125 | 45 | 2569 | 35 |
| 20 lb. in 1951 and 1953 | 3538 | 89 | 2942 | 128 | 3923 | 69 | 4384 | 77 | 2714 | 55 |
| 10 lb. in 1951, 1952, 1953 and 1954 | 3745 | 118 | 2800 | 110 | 4295 | 82 | 4473 | 84 | 2719 | 36 |
| 15 lb. in 1951, 1952, 1953 and 1954 | 3778 | 123 | 2951 | 91 | 4293 | 74 | 4443 | 116 | 2729 | 30 |
| 25 lb. in 1951, 1952, 1953 and 1954 | 3872 | 189 | 3072 | 129 | 4398 | 96 | 4774 | 160 | 3041 | 60 |
| 40 lb. in 1951, 1952, 1953 and 1954 | 3953 | 184 | 3039 | 145 | 4364 | 89 | 4680 | 149 | 3007 | 58 |
| L.S.D. (5%) | 365 | 27 | 429 | 35 | 441 | 23 | 514 | 30 | 380 | N.S. |

TABLE 2.—BORON CONTENT OF ALFALFA AS RELATED TO RATES AND FREQUENCY OF BORAX APPLICATION TO ST. PACÔME SANDY LOAM (COMPOSITE SAMPLES OF TWO CUTTINGS EVERY YEAR)

| Treatment | B in alfalfa (p.p.m. on over-dry matter basis) | | | | |
|---|---|---|---|---|---|
| Lb. of borax per acre | 1952 | 1953 | 1954 | 1955 | 1956 |
| Check | 12 | 14 | 11 | 7 | 8 |
| 15 lb. in 1951 | 18 | 15 | 9 | 7 | 6 |
| 25 lb. in 1951 | 22 | 11 | 12 | 9 | 9 |
| 40 lb. in 1951 | 37 | 20 | 15 | 12 | 10 |
| 20 lb. in 1951 and 1953 | 18 | 29 | 20 | 17 | 8 |
| 10 lb. in 1951, 1952, 1953 and 1954 | 23 | 20 | 28 | 17 | 11 |
| 15 lb. in 1951, 1952, 1953 and 1954 | 20 | 26 | 21 | 19 | 15 |
| 25 lb. in 1951, 1952, 1953 and 1954 | 28 | 35 | 36 | 23 | 21 |
| 40 lb. in 1951, 1952, 1953 and 1954 | 34 | 47 | 41 | 30 | 19 |

## RESULTS AND DISCUSSION

### *Yields of Alfalfa Hay and Seed*

As shown in Table 1, the addition of 15, 25 and 40 lb. of borax in 1951 resulted in significant yield increases of hay and seed in 1952. In 1953, only the 40-lb. rate was effective for the hay crop, and no yield increases were obtained from these treatments with either hay or seed in the following years. The moisture content of the soil was not abnormally high in any one of those years, except in 1953, which was the only year during which boron deficiency symptoms were not observed, even on the check plots. Splitting the 40-lb. rate into two and four annual applications, instead of using the same amount in one initial application, resulted in longer lasting effects and increased total yields, especially for seed production. Annual applications of 15, 25 and 40 lb. of borax per acre for 4 years, i.e. from 1951 to 1954, brought about consistent increases in both hay and seed until 1956. In that year, however, none of these treatments had any effect on the yield of seed, and the hay crop responded only to the 25- and 40-lb. rates. Therefore, it appears that borax, even when applied annually for several years, did not accumulate in soil.

### *Boron Content in Plants*

The boron content of alfalfa as related to soil treatments and yields is given in Table 2. All levels of boron in tissues associated with yield increases were above 16 parts per million. On the other hand, the highest boron content found in plants which did not receive any boron was 14 parts per million, whereas that of plants which failed to respond to an application of that element was 15 parts per million, except for one instance in 1954 where a concentration of 20 parts per million was found. These critical levels of 14 and 15 parts per million are slightly higher than those reported previously (8). Such slightly different results could be attributed to the variable degree of maturity of the plants at the time of harvesting. In the present work all plants were harvested at the early heading stage of growth, whereas in the work reported previously most of the material had been harvested at a later stage of maturity. Moreover, the data of Table 2 represent the average values for two cuttings. Since boron is more likely to be deficient on the second cutting of alfalfa than on the first, it is believed that the compositing of both cuttings for chemical analysis has also contributed in raising the so-called critical contents of boron in alfalfa. However, in 1955, the check plots, and some of those which had not received any borax since 1951, exhibited some severe symptoms of boron deficiency even on the first cutting.

### *Boron Content of Surface Soil*

The water-soluble and total boron contents of the plough-layer, from 1952 to 1956 inclusive, are given in Table 3. All levels of water-soluble boron of 0.15 part per million and less failed to give significant yield increases, and all levels of 0.35 and more were effective in improving plant growth. But the response of alfalfa to levels of water-soluble boron falling between those limits was very inconsistent, depending on the time elapsed since the

TABLE 3.–TOTAL & WATER-SOLUBLE BORON AT THE 0 TO 8-IN. DEPTH OF ST. PACÔME SANDY LOAM AS AFFECTED BY RATES & FREQUENCY OF BORAX APPLICATION

| Treatment | Water-soluble B (p.p.m.) | | | | | Total B (p.p.m.) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Lb. of borax per acre | 1952 | 1953 | 1954 | 1955 | 1956 | 1952 | 1953 | 1954 | 1955 | 1956 |
| Check | 0.20 | 0.1 | 0.15 | 0.10 | 0.1 | 4.4 | 4.5 | 4.6 | 3.1 | 3.4 |
| 15 lb. in 1951 | 0.20 | 0.25 | 0.20 | 0.20 | 0.05 | 3.8 | 4.2 | 3.2 | 4.0 | 3.5 |
| 25 lb. in 1951 | 0.45 | 0.25 | 0.30 | 0.15 | 0.15 | 4.1 | 3.8 | 3.6 | 3.6 | 4.2 |
| 40 lb. in 1951 | 0.60 | 0.35 | 0.20 | 0.20 | 0.15 | 4.4 | 4.6 | 4.2 | 3.8 | 4.0 |
| 20 lb. in 1951 and 1953 | 0.35 | 1.0 | 0.30 | 0.25 | 0.10 | 3.7 | 4.6 | 4.2 | 4.0 | 3.4 |
| 20 lb. in 1951, 1952, 1953 and 1954 | 0.55 | 0.70 | 0.75 | 0.40 | 0.10 | 4.9 | 5.0 | 4.9 | 4.3 | 4.0 |
| 15 lb. in 1951, 1952, 1953 and 1954 | 0.90 | 0.75 | 0.75 | 0.50 | 0.10 | 5.2 | 4.5 | 5.1 | 3.9 | 3.8 |
| 25 lb. in 1951, 1952, 1953 and 1954 | 1.1 | 0.75 | 1.0 | 0.55 | 0.20 | 6.1 | 6.8 | 6.3 | 5.0 | 4.1 |
| 40 lb. in 1951, 1952, 1953 and 1954 | 1.5 | 1.0 | 1.1 | 0.50 | 0.20 | 5.7 | 6.3 | 6.5 | 5.2 | 4.2 |
| pH (average of all treatments) | 6.25 | 6.35 | 6.20 | 6.30 | 6.20 | 6.25 | 6.35 | 6.20 | 6.30 | 6.00 |

TABLE 4.–TOTAL AND WATER–SOLUBLE BORON AT VARIOUS DEPTHS OF ST. PACÔME SANDY LOAM IN FALL OF 1956 AS AFFECTED BY RATES AND FREQUENCY OF BORAX APPLICATION

| Treatment | Water-soluble B (p.p.m.) | | | | Total B (p.p.m.) | | | |
|---|---|---|---|---|---|---|---|---|
| Lb. of borax per acre | 0–8″ | 8″–16″ | 16″–24″ | 24″–36″ | 0–8″ | 8″–16″ | 16″–24″ | 24″–36″ |
| Check | 0.1 | Traces | Nil | Nil | 3.4 | 2.6 | 1.4 | 1.4 |
| 15 lb. in 1951 | 0.05 | Traces | Nil | Nil | 3.5 | 3.1 | 1.6 | 1.3 |
| 25 lb. in 1951 | 0.15 | Traces | Nil | Nil | 4.2 | 2.3 | 1.8 | 1.0 |
| 40 lb. in 1951 | 0.15 | 0.05 | Nil | Nil | 4.0 | 2.8 | 1.3 | 1.2 |
| 20 lb. in 1951 and 1953 | 0.1 | Traces | Traces | Traces | 3.4 | 2.7 | 1.5 | 1.1 |
| 10 lb. in 1951, 1952, 1953 and 1954 | 0.1 | 0.05 | Traces | 0.15 | 3.5 | 2.4 | 1.9 | 1.2 |
| 15 lb. in 1951, 1952, 1953 and 1954 | 0.1 | 0.05 | 0.10 | 0.35 | 3.8 | 2.6 | 1.7 | 1.5 |
| 25 lb. in 1951, 1952, 1953 and 1954 | 0.20 | 0.05 | 0.15 | 0.25 | 3.6 | 3.0 | 1.5 | 1.6 |
| 40 lb. in 1951, 1952, 1953 and 1954 | 0.20 | 0.10 | 0.25 | 0.45 | 3.6 | 2.9 | 1.7 | 1.8 |
| pH (average of all treatments) | 6.20 | 5.92 | 5.90 | 6.00 | 6.20 | 5.90 | 5.90 | 6.00 |

last application of borax and consequently the depth of penetration of that fertilizer. Consequently, soil analysis of the plough-layer, especially if borax has been applied in the past, might indicate a deficiency of boron, when actually it could be in sufficient supply at lower depths to supply the needs of a deep-rooted crop like alfalfa. From the data obtained by analysing the plough-layer for total boron, borax, even when applied annually for 4 years, did not seem to have accumulated to any appreciable extent in that part of the profile. Therefore, apart from the amounts of boron taken up by plants, most of it has moved down to the lower depths. No relationship was found between the total boron content of the plough-layer and all other layers sampled and the growth of alfalfa.

*Boron Content of Soil at Various Depths*

In order to obtain some information on the movement and accumulation of boron within the soil profile, plots were sampled in the fall of 1956 at various depths. The following layer-samples were thus obtained: 0 to 8 inches; 8 to 16; 16 to 24; and 24 to 36. These were analysed for water-soluble and total boron, and the figures obtained are given in Table 4.

None of the boron applied in 1951, regardless of the rate used, was left in the surface 36 inches of soil, either as water-soluble or total. The same applied to the 20-lb. application made in 1953. The distribution of water-soluble boron in the soil profile in the fall of 1956, for the plots having received borax annually from 1951 to 1954 inclusive, varied considerably, depending upon the rate used. The only water-soluble boron left from a 10-lb. application was found in the 24- to 36-inch depth, whereas from the 15-lb. application some was found also in the 16- to 24-inch depth. With higher rates of borax application, i.e. 25 and 40 lb. per acre, some water-soluble boron was left in the profile, the highest concentrations being found at the lower depths, especially between the 24- and 36-inch levels. However, the amounts of residual boron in water-soluble form represented only a small portion of the amounts added. Since the corresponding figures for total boron are not much higher than those recorded on the check plots, it must be concluded that most of the borax applied, (approximately 65 per cent for the 10- and 15-lb. rates and 75 per cent for the higher rates) had moved below the 36-inch depths, i.e. past the zone of most intense root activity. Very little fixation, if any, of boron occurred between the surface and the 36-inch depth.

Considering the yield data and boron content of the soil, it appears that most of the borax applied to St. Pacôme sandy loam, regardless of the rate used, has moved below the root zone in approximately 2 years. Also, more borax was required by alfalfa for seed than for hay production. Therefore, it is believed that for the cultivation of alfalfa on Quebec soils similar to St. Pacôme sandy loam, borax should be applied every 2 years at rates ranging between 15 and 20 lb. per acre for hay and 25 to 30 lb. for seed. It must be remembered, however, that borax may be toxic to the nurse crop if used at seeding time in too high amounts. Consequently, it is advisable to delay the application of any amount of borax greater than 20 lb. per acre until the nurse crop has been removed.

## ACKNOWLEDGEMENTS

The author wishes to express his thanks to R. Baril, Soil Surveyor, Canada Department of Agriculture, for guidance in matters of soil type location and description and to K. F. Nielsen, Field Husbandry Division, Ottawa, for helpful criticism of the manuscript.

## REFERENCES

1. Askew, H. O., R. H. K. Thompson, and E. Chittendem. Effect of borax top-dressing on boron status of soil and fruit. New Zealand J. Sci. Technol. 20:74A-78A. 1938.
2. Berger, K. C., and E. Truog. Boron tests and determination for soils and plants. Soil Sci. 57:25-36. 1944.
3. Berger, K. C., and E. Truog. Boron availability in relation to soil reaction and organic matter content. Soil Sci. Soc. Amer. Proc. 10:113-116. 1945.
4. Brown, B. A., R. I. Munsell, and A. V. King. Potassium and boron fertilization of alfalfa on a few Connecticut soils. Soil Sci. Soc. Amer. Proc. 10:134-140. 1945.
5. Crafts, A. S., and R. N. Raynor. The herbicidal properties of boron compounds. Hilgardia 10:343-374. 1936.
6. Krugel, C., C. Dreyspring, and R. Lotthammer. Leaching experiments with borates. Superphosphate 11:141-156. 1938.
7. Kubota, J., K. C. Berger, and E. Truog. Boron movement in soils. Soil Sci. Soc. Amer. Proc. 13:130-134. 1948.
8. Ouellette, G. J., and R. O. Lachance. Soil and plant analysis as means of diagnosing boron deficiency in alfalfa in Quebec. Can. J. Agr. Sci. 34:494-503. 1954.
9. Reeve, E., A. L. Prince, and F. E. Bear. The boron needs of New Jersey soils. New Jersey Agr. Expt. Sta. Bull. 709. 1944.
10. Wilson, C. M., R. O. Lovvorn, and W. W. Woodhouse. Movement and accumulation of water-soluble boron within the soil profile. Agron. J. 43:363-367. 1951.
11. Woodbridge, C. G. The boron content of some Okanagan soils. Sci. Agr. 20:257-265. 1940.

# Ca:Mg RATIOS IN SOIL AND THE YIELD AND COMPOSITION OF ALFALFA[1]

R. L. Halstead, A. J. MacLean and K. F. Nielsen

*Canada Department of Agriculture, Ottawa, Ontario*

[Received for publication December 3, 1957

## ABSTRACT

When carbonates of magnesium or calcium were added to surface samples of four acid soils to establish a range in exchangeable Ca:Mg ratios, magnesium carbonate reduced exchangeable calcium and, with one exception, calcium carbonate reduced exchangeable magnesium. Corresponding reductions of water-soluble magnesium and calcium occurred in two of the soils. For a given amount of the cation in exchangeable form, there was more magnesium than calcium in water-soluble form. The carbonate treatments had no effect on exchangeable potassium but usually reduced water-soluble potassium. The exchangeable Ca:Mg ratios in the different soils varied from 0.6:1.0 to 1.5:1.0 where magnesium carbonate was applied, and from 4.1:1.0 to 13.5:1.0 where calcium carbonate was used.

Yields of alfalfa grown in the soils increased with addition of carbonates. The width of the Ca:Mg ratio in the treated samples had no significant effect on yield except in one soil where the pH was raised to slightly above the neutral point. Magnesium carbonate reduced calcium in the plants more than calcium carbonate reduced magnesium. With addition of potassium, the percentage reduction of plant magnesium was greater than that of calcium. Values for sum of cations in the plants were reduced by the magnesium carbonate treatment and usually by addition of potassium. The carbonate of calcium tended to be slightly more effective than that of magnesium in increasing the phosphorus content of the plants.

From the standpoint of alfalfa yield, it is suggested that a magnesian limestone may be expected to be a satisfactory corrective of acidity, even though the resulting Ca:Mg ratio in the soil may be relatively low.

## INTRODUCTION

The exchangeable Ca:Mg ratio in soil in relation to growth of alfalfa became of interest when the question arose as to whether dolomitic or calcitic limestone might be expected to be equally effective in acid soils possessing relatively low Ca:Mg ratios. Accordingly, in 1955, a greenhouse experiment was initiated in which alfalfa was grown in four soils pre-treated with carbonates of calcium or magnesium to alter the Ca:Mg ratio.

Following Loew's (9) proposal that a certain Ca:Mg ratio in the soil was required for optimum growth of plants, a number of publications relating to this topic appeared in the literature. In a critical review, Lipman (8) concluded that there was little or no evidence in support of the necessity of a specific Ca:Mg ratio for plant growth. Moser (11), employing soils with Ca:Mg ratios varying from 1:1 to 4.50:1, found no significant correlation between Ca:Mg ratio and crop yields. Bear and Toth (1) in giving proportions of different cations on the exchange material of an ideal soil, suggested a Ca:Mg ratio of 6.5:1. Hunter (5) found, however, that the yield of alfalfa was not influenced by variations from 1:4 to 32:1 in the Ca:Mg ratio in the soil.

[1] Joint contribution from Chemistry Division, Science Service (Contribution No. 386), and Field Husbandry Division, Experimental Farms Service, Canada Department of Agriculture, Ottawa, Ont.

In the present paper, the exchangeable and water-soluble cation content of the soils treated with carbonates of calcium or magnesium are discussed in relation to the yield and composition of alfalfa grown in the soils with and without phosphorus and potassium fertilizers. As a further measure of the influence of the carbonate treatments on availability of phosphorus, the amounts of acid-soluble and $NaHCO_3$-soluble phosphorus extracted from the soils are presented.

## EXPERIMENTAL PROCEDURE

Two surface samples of Bearbrook clay loam, one of Uplands sand and one of Mountain sandy loam, were collected from the Ottawa district. The Bearbrook, Uplands and Mountain series belong to the Dark Grey Gleisolic, Podsol, and Brown Podsolic great soil groups, respectively, and have been described elsewhere (4). The fields selected for sampling were managed in rotations consisting of oats followed by a number of years of hay. None of the fields had been limed and none had received heavy applications of fertilizer.

The samples were air-dried, passed through a half-inch mesh sieve, mixed and placed in glazed gallon pots on a volume basis. The amounts of lime required to raise the pH of the soils to about the neutral point were determined by the method of Dunn (3). On this basis, the required amount of calcium carbonate or magnesium carbonate was mixed throughout the soil to provide the following treatments: 1) check; 2) $MgCO_3$; 3) $CaCO_3$. The soils were kept moist by surface applications of water as required. Three pots of each soil representing the above treatments were maintained in the moist condition for a period of 4 months, after which the samples were air-dried, passed through a 2-mm. sieve and retained for analysis.

After a period of 30 days from the time of incorporation of the carbonates, fertilizer treatments were applied to the remainder of the experiment in a layer at a depth of 2 inches. These treatments were: 1) potassium chloride at the rate of 200 lb. $K_2O$ per acre; 2) calcium dihydrogen phosphate at the rate of 200 lb. $P_2O_5$ per acre; 3) a combination of 1) and 2). The treatments were randomized and were replicated five times. Inoculated Grimm alfalfa was seeded and later thinned to ten plants per pot. Four crops of alfalfa in the bloom stage were harvested.

Composite samples of the alfalfa from the five replicates of each treatment were ground in a Wiley mill and organic matter was destroyed by digestion with sulphuric, nitric and perchloric acids, as described by Piper (14). Phosphorus was determined by the method of King (7). Calcium and potassium were determined by the method described by Peech *et al.* (13). After separation of the calcium, magnesium was determined by titration with versene as described by Cheng and Bray (2).

The pH of the soil was determined by means of a glass electrode using a 1:1 soil:water ratio. Exchange capacity and exchangeable calcium and potassium were determined according to the procedures of Peech *et al.* (13). Exchangeable magnesium in the extract was determined by titration with versene (2) after separation of calcium. Water-soluble calcium, magnesium and potassium were extracted by shaking a 1:2.5 soil:water suspension

for a 24-hour period. The procedures for determining calcium, magnesium and potassium in the extracts were similar to those employed for the cations in exchangeable form. Acid-soluble phosphorus was determined by the method of Truog (15) and $NaHCO_3$-soluble phosphorus by the method of Olsen *et al.* (12).

## RESULTS AND DISCUSSION

### *Effect of Carbonate Treatments on Soil Properties*

The comparative effects of carbonates of calcium and magnesium on exchange properties of the soils are shown by the data in Table 1. The magnesium carbonate treatment decreased exchangeable calcium in the soils. Addition of calcium carbonate resulted in corresponding decreases in exchangeable magnesium in all soils except Uplands sand, where a small amount of magnesium carbonate was included with the calcium carbonate treatment. In a previous publication (10), calcium hydroxide was shown to have a repressive effect on exchangeable magnesium. The carbonates had no consistent effect on exchangeable potassium.

Although the two treatments contained the same amounts of calcium or magnesium on the equivalent basis, the increases in exchangeable calcium resulting from additions of calcium carbonate were greater than the corresponding increases in exchangeable magnesium obtained with magnesium carbonate. The trends for higher degree of base saturation of the soils and for slightly higher pH values for three of the soils show that the carbonate of calcium was more effective than that of magnesium in neutralizing acidity of the soils. The amount of carbonates added to Mountain sandy loam exceeded that required to neutralize the soil.

TABLE 1.—EXCHANGEABLE CATION CONTENT OF SOILS TREATED WITH CARBONATES OF CALCIUM OR MAGNESIUM

| Carbonate treatment | Rate per acre[1] | pH | Exchangeable bases | | | | Exchange capacity | Base saturation |
|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | K | Ca:Mg ratio | | |
| | lb. | | me./100 gm. | | | | me./100 gm. | % |
| | | | Uplands sand | | | | | |
| Check | — | 5.9 | 3.5 | 0.5 | 0.16 | 7.0 | 7.0 | 59 |
| $MgCO_3$ | 2,520 | 6.8 | 3.2 | 2.2 | 0.13 | 1.5 | — | 79 |
| $CaCO_3$[2] | 2,804 | 6.9 | 5.9 | 0.5 | 0.12 | 11.8 | — | 93 |
| | | | Mountain sandy loam | | | | | |
| Check | — | 5.8 | 4.1 | 1.2 | 0.22 | 3.4 | 9.6 | 58 |
| $MgCO_3$ | 7,980 | 7.1 | 3.8 | 6.4 | 0.22 | 0.6 | — | 109 |
| $CaCO_3$ | 9,500 | 7.3 | 10.8 | 0.8 | 0.20 | 13.5 | — | 123 |
| | | | Bearbrook clay loam (C) | | | | | |
| Check | — | 4.9 | 8.8 | 4.1 | 0.34 | 2.1 | 24.5 | 54 |
| $MgCO_3$ | 9,660 | 6.2 | 8.3 | 11.0 | 0.38 | 0.8 | — | 80 |
| $CaCO_3$ | 11,500 | 6.3 | 16.7 | 3.6 | 0.34 | 4.6 | — | 84 |
| | | | Bearbrook clay loam (D) | | | | | |
| Check | — | 5.5 | 10.4 | 5.2 | 0.31 | 2.0 | 22.8 | 70 |
| $MgCO_3$ | 7,980 | 6.7 | 9.5 | 10.7 | 0.32 | 0.9 | — | 90 |
| $CaCO_3$ | 9,500 | 6.7 | 17.3 | 4.2 | 0.37 | 4.1 | — | 96 |

[1] The equivalents of Ca or Mg added to any one soil are similar.
[2] $MgCO_3$ (165 lb. per acre) was added to the $CaCO_3$ treatment to ensure a supply of some available magnesium in this treatment.

TABLE 2.—WATER-SOLUBLE CATION CONTENT OF SOILS TREATED WITH CARBONATES OF CALCIUM OR MAGNESIUM

| Carbonate treatment | Water-soluble bases | | | |
|---|---|---|---|---|
| | Ca | Mg | K | Ca:Mg ratio |
| | me./100 gm. | | | |
| | Uplands sand | | | |
| Check | 0.15 | 0.07 | 0.028 | 2.1 |
| $MgCO_3$ | 0.13 | 0.22 | 0.025 | 0.6 |
| $CaCO_3$ | 0.24 | 0.07 | 0.025 | 3.4 |
| | Mountain sandy loam | | | |
| Check | 0.32 | 0.20 | 0.046 | 1.6 |
| $MgCO_3$ | 0.20 | 0.83 | 0.034 | 0.2 |
| $CaCO_3$ | 0.81 | 0.09 | 0.036 | 9.0 |
| | Bearbrook clay loam (C) | | | |
| Check | 0.29 | 0.28 | 0.017 | 1.0 |
| $MgCO_3$ | 0.23 | 0.54 | 0.011 | 0.4 |
| $CaCO_3$ | 0.60 | 0.22 | 0.011 | 2.7 |
| | Bearbrook clay loam (D) | | | |
| Check | 0.17 | 0.17 | 0.019 | 1.0 |
| $MgCO_3$ | 0.32 | 0.52 | 0.020 | 0.6 |
| $CaCO_3$ | 0.40 | 0.17 | 0.015 | 2.4 |

The Ca:Mg ratios established in the soils varied from 0.6 to 1.5 where magnesium carbonate was applied, and from 4.1 to 13.5 where calcium carbonate was employed.

The effect of calcium carbonate on water-soluble magnesium and of magnesium carbonate on water-soluble calcium (Table 2) was less consistent on the different soils than the corresponding effect on exchangeable calcium and magnesium (Table 1). On Mountain sandy loam and Bearbrook clay loam (C), however, there were trends for calcium carbonate to reduce water-soluble magnesium and for magnesium carbonate to reduce water-soluble calcium. In all but one instance, additions of carbonates reduced water-soluble potassium.

In contrast with the results reported for exchangeable cations, the increases in water-soluble magnesium with addition of magnesium carbonate were fully as great as were the increases in water-soluble calcium resulting from application of calcium carbonate. Ca:Mg ratios were lower for the water-soluble than for the exchangeable form. It would appear that, for a given amount of exchangeable calcium and magnesium, more magnesium than calcium is found in the water-soluble form.

The influence of the carbonate treatments on soluble soil phosphorus varied with the method of extracting the phosphorus (Table 3). Carbonates of calcium or magnesium increased the acid-soluble phosphorus in the soils. Magnesium carbonate tended to give slightly higher acid-soluble phosphorus values than did calcium carbonate, except on Uplands sand

TABLE 3.—SOLUBLE PHOSPHORUS CONTENT OF SOILS TREATED WITH CARBONATES OF CALCIUM OR MAGNESIUM

| Carbonate treatment | pH | Soluble phosphorus | | pH | Soluble phosphorus | |
|---|---|---|---|---|---|---|
| | | Acid | $NaHCO_3$ | | Acid | $NaHCO_3$ |
| | | p.p.m. | p.p.m. | | p.p.m. | p.p.m. |
| | Uplands sand | | | Bearbrook clay loam (C) | | |
| Check | 5.9 | 24 | 16 | 4.9 | 23 | 10 |
| $MgCO_3$ | 6.8 | 29 | 13 | 6.2 | 28 | 11 |
| $CaCO_3$ | 6.9 | 33 | 15 | 6.3 | 27 | 12 |
| | Mountain sandy loam | | | Bearbrook clay loam (D) | | |
| Check | 5.8 | 34 | 10 | 5.5 | 60 | 9 |
| $MgCO_3$ | 7.1 | 47 | 10 | 6.7 | 63 | 10 |
| $CaCO_3$ | 7.3 | 44 | 12 | 6.7 | 61 | 13 |

TABLE 4.—TOTAL YIELD OF FOUR ALFALFA CROPS GROWN IN SOIL SAMPLES VARYING IN Ca:Mg RATIO

| Carbonate treatment | Ca:Mg ratio (exchangeable) | Yield of alfalfa per gallon pot | | | |
|---|---|---|---|---|---|
| | | K added | P added | PK added | L.S.D. (0.05) |
| | | gm. | gm. | gm. | gm. |
| | Uplands sand | | | | |
| Check | 7.0 | 29.1 | 27.7 | 37.0 | |
| $MgCO_3$ | 1.5 | 32.5 | 32.2 | 42.9 | |
| $CaCO_3$ | 11.8 | 35.2 | 35.5 | 41.1 | 4.2 |
| | Mountain sandy loam | | | | |
| Check | 3.4 | 13.1 | 21.0 | 27.7 | |
| $MgCO_3$ | 0.6 | 18.5 | 25.6 | 36.3 | |
| $CaCO_3$ | 13.5 | 28.9 | 31.2 | 36.0 | 4.0 |
| | Bearbrook clay loam (C) | | | | |
| Check | 2.1 | 23.2 | 36.5 | 38.7 | |
| $MgCO_3$ | 0.8 | 39.8 | 49.7 | 50.7 | |
| $CaCO_3$ | 4.6 | 39.1 | 47.4 | 53.2 | 3.3 |
| | Bearbrook clay loam (D) | | | | |
| Check | 2.0 | 27.1 | 41.0 | 44.0 | |
| $MgCO_3$ | 0.9 | 40.5 | 48.7 | 54.9 | |
| $CaCO_3$ | 4.1 | 38.4 | 47.3 | 52.2 | 5.4 |

where a small amount of magnesium carbonate was included with the calcium carbonate treatment. Application of calcium carbonate resulted in higher amounts of $NaHCO_3$-soluble phosphorus in the soils than were obtained with magnesium carbonate. Three of the soils treated with calcium carbonate contained more $NaHCO_3$-soluble phosphorus than was found in the untreated soils.

*Yield and Composition of Alfalfa*

The data in Table 4 show that magnesium carbonate or calcium carbonate increased the yield of alfalfa. The differences were significant, except in two instances on Uplands sand. The kind of carbonate used and the resulting variation in the Ca:Mg ratio established in the soil had no significant effect on the yield of alfalfa grown in Uplands sand and Bearbrook clay loam. But on Mountain sandy loam, where the amounts of carbonates applied were slightly in excess of those required to neutralize the soil, the yields of alfalfa grown with phosphorus or potassium applied singly were considerably lower where magnesium carbonate was applied than where calcium carbonate was used. The differences were significant.

Comparison of the data for the K and PK treatments shows that the addition of phosphorus increased the yield significantly on all soils. Application of potassium increased the yield significantly on Uplands sand and Mountain sandy loam and in two instances on Bearbrook clay loam, as shown by the data for the P and PK treatments. On Uplands sand and Mountain sandy loam, the yield responses to fertilizer tended to be greater on samples treated with magnesium carbonate than on those receiving calcium carbonate.

Table 5 gives the composition of alfalfa as influenced by the carbonate and fertilizer treatments. Calcium carbonate increased calcium and in most instances decreased magnesium in the plants, whereas magnesium

TABLE 5.—COMPOSITION OF ALFALFA

| Carbonate treatment | Cation content | | | | | | Phosphorus content | |
|---|---|---|---|---|---|---|---|---|
| | P added | | | PK added | | | K added | PK added |
| | Ca | Mg | K | Ca | Mg | K | | |
| | me./100 gm. | | | | | | % | % |
| | Uplands sand | | | | | | | |
| Check | 106 | 47 | 24 | 88 | 36 | 37 | 0.25 | 0.29 |
| $MgCO_3$ | 82 | 66 | 19 | 71 | 46 | 37 | 0.25 | 0.27 |
| $CaCO_3$ | 114 | 43 | 19 | 95 | 35 | 40 | 0.24 | 0.29 |
| | Mountain sandy loam | | | | | | | |
| Check | 85 | 47 | 33 | 79 | 36 | 48 | — | 0.22 |
| $MgCO_3$ | 44 | 73 | 31 | 46 | 46 | 38 | 0.21 | 0.24 |
| $CaCO_3$ | 110 | 46 | 28 | 98 | 39 | 36 | 0.24 | 0.29 |
| | Bearbrook clay loam (C) | | | | | | | |
| Check | 85 | 53 | 28 | 72 | 45 | 39 | 0.16 | 0.21 |
| $MgCO_3$ | 62 | 63 | 20 | 51 | 60 | 28 | 0.18 | 0.26 |
| $CaCO_3$ | 103 | 48 | 19 | 89 | 39 | 27 | 0.21 | 0.26 |
| | Bearbrook clay loam (D) | | | | | | | |
| Check | 74 | 43 | 37 | 78 | 36 | 47 | 0.15 | 0.20 |
| $MgCO_3$ | 60 | 53 | 37 | 63 | 45 | 39 | 0.18 | 0.22 |
| $CaCO_3$ | 89 | 38 | 39 | 81 | 29 | 43 | 0.21 | 0.26 |

TABLE 6.—RATIOS AND TOTAL EQUIVALENTS OF CATIONS IN ALFALFA

| Carbonate treatment | Cation equivalent ratios | | | | Sum of cations (Ca+Mg+K) | | Mg:P ratio | |
|---|---|---|---|---|---|---|---|---|
| | Ca:Mg | | (Ca+Mg):K | | | | | |
| | P | PK | P | PK | P | PK | K | PK |
| | | | | | me./100 gm. | | | |
| | Uplands sand | | | | | | | |
| Check | 2.3 | 2.4 | 6.4 | 3.4 | 177 | 161 | 0.8 | 0.8 |
| $MgCO_3$ | 1.2 | 1.5 | 7.8 | 3.2 | 167 | 154 | 1.2 | 1.0 |
| $CaCO_3$ | 2.6 | 2.7 | 8.3 | 3.3 | 176 | 170 | 1.0 | 0.8 |
| | Mountain sandy loam | | | | | | | |
| Check | 1.8 | 2.2 | 4.0 | 2.4 | 165 | 163 | — | 1.0 |
| $MgCO_3$ | 0.6 | 1.0 | 3.8 | 2.4 | 148 | 130 | 1.4 | 1.2 |
| $CaCO_3$ | 2.4 | 2.5 | 5.6 | 3.8 | 184 | 173 | 0.8 | 0.8 |
| | Bearbrook clay loam (C) | | | | | | | |
| Check | 1.6 | 1.6 | 4.9 | 3.0 | 166 | 156 | 1.5 | 1.3 |
| $MgCO_3$ | 1.0 | 0.9 | 6.3 | 4.0 | 145 | 139 | 2.1 | 1.4 |
| $CaCO_3$ | 2.1 | 2.3 | 7.9 | 4.7 | 170 | 155 | 1.2 | 0.9 |
| | Bearbrook clay loam (D) | | | | | | | |
| Check | 1.7 | 2.2 | 3.2 | 2.4 | 154 | 161 | 1.1 | 1.1 |
| $MgCO_3$ | 1.1 | 1.4 | 3.1 | 2.8 | 150 | 147 | 1.5 | 1.3 |
| $CaCO_3$ | 2.3 | 2.8 | 3.3 | 2.6 | 166 | 153 | 0.9 | 0.7 |

carbonate increased magnesium and decreased the calcium content. In most instances, the potassium content of the plants decreased with addition of carbonates. Addition of potassium increased the concentration of potassium in the plants, decreased magnesium, and with three exceptions decreased the calcium content. The direct effect of the added cations on the cation content of the plants cannot be separated from the influence of yield differences where such occurred with addition of carbonates or potassium.

Except on Uplands sand, the carbonate treatments increased the phosphorus content of the alfalfa. Usually calcium carbonate was more effective than magnesium carbonate in increasing the phosphorus content. This tendency for a more favourable influence of the carbonate of calcium than that of magnesium on the phosphorus content does not lend support to the theory that magnesium acts as a phosphate carrier and facilitates the uptake of phosphorus by the plant. In a recent review Jacob (6) cites numerous findings that support the theory. In the present study of the possible effect of low Ca:Mg ratios, no magnesium deficiency was anticipated and presumably the supply of magnesium in the soils treated with either carbonate was adequate for uptake of phosphorus. As shown previously (Table 3), the soils receiving calcium carbonate contained higher amounts of $NaHCO_3$-soluble phosphorus than did the samples treated with magnesium carbonate.

The relative variation in the amounts of the different cations as well as phosphorus in the plants in relation to carbonate and fertilizer treatments is shown by the data in Table 6. The Ca:Mg ratios for the plants reflect the variation in the Ca:Mg ratios established in the soils by carbonate treatments. The low Ca:Mg ratio (0.6) in alfalfa grown with applied phosphorus and an excess of magnesium carbonate in Mountain sandy loam was associated with low exchangeable and water-soluble Ca:Mg ratios in the soil and with a reduction in yield from that obtained with a corresponding excess of calcium carbonate. There was a tendency for slightly higher Ca:Mg ratios to occur with addition of potassium. This was the net result of a greater percentage reduction of magnesium than of calcium in the plants when potassium was applied.

The values for the sum of cations in the plants and in all but one instance the (Ca+Mg):K ratios were higher with calcium carbonate than with the magnesium carbonate treatment. The reduction of calcium by magnesium carbonate was greater than the corresponding reduction of magnesium by calcium carbonate. With addition of potassium, the (Ca+Mg):K ratios were reduced considerably, and the sum of cations tended to be lower than that found in the plants grown without potassium fertilizer.

The Mg:P ratios for alfalfa grown in the soils receiving the magnesium carbonate treatment were higher than the corresponding values obtained without a carbonate treatment or with addition of calcium carbonate. As already discussed, magnesium carbonate increased magnesium in the plants, whereas calcium carbonate decreased magnesium and was more effective than magnesium carbonate in increasing the phosphorus content.

It is concluded that dolomitic limestone as a corrective of soil acidity may be expected to give satisfactory results where the Ca:Mg ratios are within the range usually encountered. It is true that the composition of the plants and the nutrient status of the soil varied with the Ca:Mg ratios established in the experiment, but most of the evidence indicated that a narrow Ca:Mg ratio did not have an adverse effect on yield.

## REFERENCES

1. Bear, F. E., and S. J. Toth. Influence of calcium on availability of other soil cations. Soil. Sci. 65:69-74. 1948.
2. Cheng, K. L., and R. H. Bray. Determination of calcium and magnesium in soil and plant material. Soil Sci. 72:449-458. 1951.
3. Dunn, L. E. Lime requirement determination of soils by means of titration curves. Soil Sci. 56:341-351. 1943.
4. Hills, G. A., N. R. Richards, and F. F. Morwick. Soil survey of Carleton County. Rept. 7, Ontario Soil Survey, Guelph, Ont. 1944.
5. Hunter, A. S. Yield and composition of alfalfa as affected by variations in the calcium-magnesium ratio in the soil. Soil Sci. 67:53-62. 1949.
6. Jacob, A. Magnesium: The fifth major plant nutrient. Staples Press Ltd., London, England. 1958.
7. King, E. J. The colorimetric determination of phosphorus. Biochem. J. 26:292-297. 1932.
8. Lipman, C. B. A critique of the lime-magnesia hypothesis. Plant World 19:83-105; 119-135. 1916.
9. Loew, O., and D. W. May. The relation of lime and magnesium to plant growth. Bull. 1, Bur. Plant Ind., U.S. Dept. Agr., Washington, D.C. 1901.

10. MacLean, A. J. Influence of additions of lime to soils on the availability of potassium and other cations for alfalfa. Can. J. Agr. Sci. 36:213-220. 1956.

11. Moser, F. The calcium-magnesium ratio in soils and its relation to crop growth. J. Amer. Soc. Agron. 25:365-377. 1933.

12. Olsen, S. R., C. V. Cole, F. Watanabe, and L. A. Dean. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. Circ. 939, U.S. Dept. Agr., Washington, D.C. 1954.

13. Peech, M., L. T. Alexander, L. A. Dean, and J. F. Reed. Methods of soil analysis for soil-fertility investigations. Circ. 757, U.S. Dept. Agr., Washington, D.C. 1947.

14. Piper, C. S. Soil and plant analysis. Interscience Publishers Inc., New York, N.Y. 1944.

15. Truog, E. The determination of the readily available phosphorus of soils. J. Amer. Soc. Agron. 22:874-882. 1930.

# LEACHATES FROM CALCAREOUS SOILS AND RELATED MATERIALS[1]

R. C. Turner, W. E. Nichol and K. E. Miles

*Canada Department of Agriculture, Ottawa, Ontario*

[Received for publication April 14, 1958]

## ABSTRACT

Leaching experiments were made in the laboratory with a variety of calcareous materials. When the materials, including natural soils, were essentially free from organic matter, the pH and calcium concentrations of the leachates were roughly 9.8 and $1.3\times10^{-4}$ molar respectively. When the calcareous materials contained an appreciable amount of organic matter, the constitution of the leachates varied considerably.

## INTRODUCTION

There have been a number of papers (1, 2, 4, 6) concerning the relation between the pH of calcareous soils and the partial pressure of $CO_2$ ($P_{CO_2}$) of the soil solution. Very little has appeared, however, concerning the $P_{CO_2}$ of leachates in calcareous soils. Turner (5) on purely theoretical grounds concluded that the $P_{CO_2}$ of the leachates should be lower than that which exists in the atmosphere above ground, especially during heavy rains. In the ideal case, where nothing in the soil affects the amount of $CaCO_3$ dissolved, and the solution in passing through the soil has time to come to equilibrium with the solid $CaCO_3$, the $P_{CO_2}$, pH and $Ca^{2+}$ concentration of the leachate should be respectively about $10^{-3}$ atm., 9.9 and $1.4\times10^{-4}$M.

The objectives of the work reported here were to determine experimentally the pH and calcium concentration of leachates from a variety of calcareous materials, including calcareous soils, and to compare the results with the corresponding values for suspension of the same materials under atmospheres of known $P_{CO_2}$. The effect of calcium salts, other than $CaCO_3$, in the material was approximated by using as the leaching solution a $10^{-3}$M $CaCl_2$ solution in place of $H_2O$ in some of the experiments.

## EXPERIMENTAL

The apparatus used to measure the pH of the leachates (Figure 1) is in most respects self-explanatory. The electrodes were sealed into the cell with de Khotinsky cement. The long capillary used for the outlet essentially eliminated back diffusion of $CO_2$ into the cell during the leaching process. When leaching was started the stopcock at the bottom was closed and the filling tube was left open. When the leachate in the cell was at the desired height, the filling tube was sealed off and the stopcock at the bottom opened. This allowed continuous leaching while the level in the cell remained constant. The rate of flow of solution through the column was maintained at about 50 ml. per hour by means of the stopcock at the bottom. The pH of the leachate in the cell was measured inter-

[1] Contribution No. 395, Chemistry Division, Science Service, Canada Department of Agriculture, Ottawa, Ont.

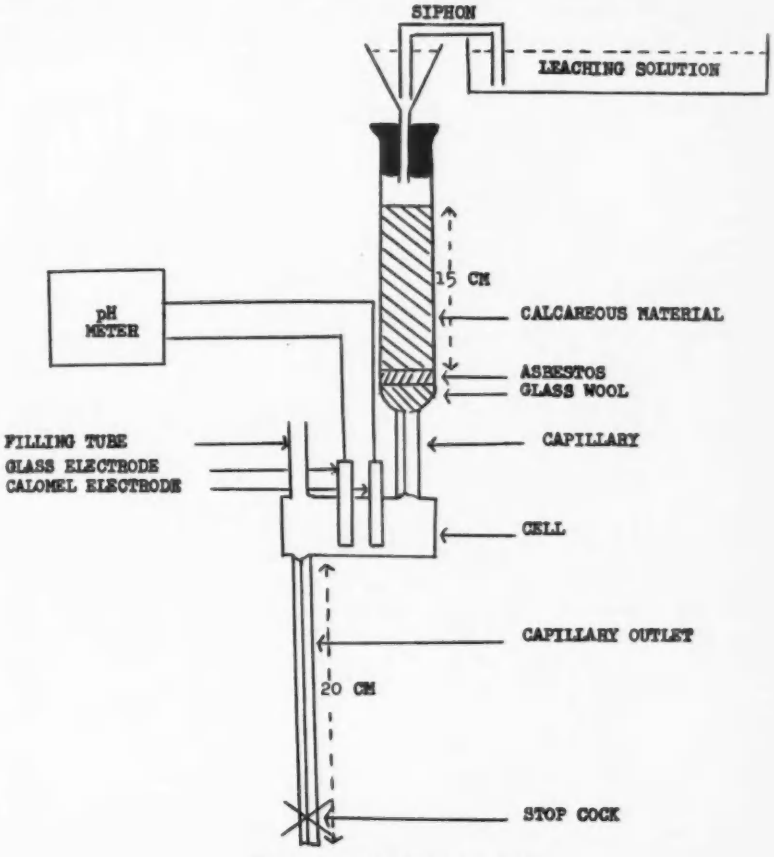



FIGURE 1.—Leaching apparatus.

mittently until there was no change in pH over several hours indicating that, among other things, the air in the cell had come to the same $P_{CO_2}$ as the leachate leaving the column. At this time a sample of leachate was collected from the outlet tube and the final pH was recorded. The filling tube was then punctured to allow the leachate to run out of the cell and the funnel at the top of the column was replaced with a stopper. The cell was then washed with water and filled with a standard buffer solution to determine any correction, if necessary, that had to be applied to the recorded pH value. The leachates were analysed for calcium and magnesium.

The materials were leached with water for 24 hours, except where otherwise stated. After this, the materials were removed from the columns and air dried. The air-dry samples were mixed with water (solid/water 0.40) and shaken continuously for 48 hours under an atmosphere with a

TABLE 1.—DESCRIPTION OF CALCAREOUS MATERIALS USED IN THE COLUMNS

| Material | C.E.C. me./100 gm. | Loss on ignition at 450°C. % | Texture | Remarks |
|---|---|---|---|---|
| Sand | — | — | — | Quartz sand; 10% $CaCO_3$ |
| Kaolin | 5.2 | — | Passed 40-mesh screen | Ca-saturated at pH 7; 10% $CaCO_3$ |
| Hydrobiotite | 49.0 | — | Passed 40-mesh screen | Ca-saturated at pH 7; 10% $CaCO_3$ |
| Vermiculite[1] | 164.0 | — | Exfoliated | Ca-saturated at pH 7; 10% $CaCO_3$ |
| Peat (a) | 125.0 | 85.7 | — | Ca-saturated at pH 7; 10% $CaCO_3$ |
| Peat (b) | 125.0 | 85.7 | — | Same as peat (a) except treated with saturated $Ca(OH)_2$ solution |
| Soil No. 1 | — | 1.54 | Fine sandy loam | Subsoil |
| Soil No. 2 | — | 1.88 | Fine sandy loam | Subsoil |
| Soil No. 3 | — | 4.05 | Silty clay loam | Surface |
| Soil No. 4 | — | 14.0 | Sandy loam | Surface; 10% $CaCO_3$ |

[1]Commercial product containing some hydrobiotite

$P_{CO_2}$ of $3\times10^{-4}$ atm. in one experiment and $5\times10^{-2}$ atm. in another. At this time, the pH values of the suspensions were measured, the suspensions filtered and the filtrates analysed for calcium and magnesium.

The materials used in the columns were calcareous soils and mixtures of clay, peat or sand with $CaCO_3$. A brief description of the materials, given in Table 1, shows that they varied extensively in exchange capacity and in organic matter content.

## RESULTS

The results from the materials essentially free from organic matter will be considered first. As shown in Table 2, with these materials the pH of each leachate was more than one unit higher than that of the corresponding suspension with a $P_{CO_2}$ of $3\times10^{-4}$ atm. With all, except Soil No. 1, the calcium concentrations in the suspensions at $P_{CO_2}$ of $3\times10^{-4}$ atm. were greater by a factor of about 5 or more than those of the corresponding leachates. When the $P_{CO_2}$ of the atmosphere over the suspensions was $5\times10^{-2}$ atm. the calcium concentrations were higher and the pH

TABLE 2.—CALCIUM AND MAGNESIUM CONCENTRATIONS AND pH OF LEACHATES AND SUSPENSIONS

| Material | Leachates | | | Suspensions | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $P_{CO_2}$ = 0.0003 atm. | | | $P_{CO_2}$ = 0.05 atm. | | |
| | pH | Ca $\times 10^3$M | Mg $\times 10^3$M | pH | Ca $\times 10^3$M | Mg $\times 10^3$M | pH | Ca $\times 10^3$M | Mg $\times 10^3$M |
| Sand | 9.80 | 0.13 | — | 8.30 | 0.60 | — | 6.96 | 1.82 | — |
| Kaolin | 9.80 | 0.13 | — | — | — | — | — | — | — |
| Hydrobiotite | 9.80 | 0.11 | trace | 8.23 | 0.82 | 0.07 | 7.08 | 3.77 | 0.47 |
| Vermiculite | 9.80 | 0.13 | trace | 8.23 | 0.92 | 0.24 | 7.09 | 3.20 | 1.30 |
| Peat (a) | 8.20 | 0.45 | trace | — | — | — | — | — | — |
| Peat (b)[1] | 9.20 | 0.18 | trace | 8.20 | 1.86 | trace | 7.11 | 6.10 | trace |
| Soil No. 1 | 9.70 | 0.14 | 0.24 | 8.60 | 0.25 | 0.86 | 7.14 | 1.87 | 4.10 |
| Soil No. 2 | 9.75 | 0.18 | 0.07 | 8.45 | 1.01 | 0.35 | 7.22 | 4.43 | 1.50 |
| Soil No. 3 | 9.30 | 0.22 | 0.10 | 8.30 | 1.53 | 0.61 | 7.19 | 4.40 | 1.80 |
| Soil No. 4 | 8.80 | 0.25 | trace | 8.44 | 1.27 | trace | 7.22 | 5.10 | 0.27 |

[1]Solid/water 0.2 in the suspensions

values lower than at the lower $P_{CO_2}$. The high magnesium relative to the calcium concentration with Soil No. 1 may indicate the presence of a dolomitic limestone in this soil. In any event, the pH and calcium plus magnesium concentrations were similar to those of the other calcareous materials in the leachates as well as in the suspensions. In general these materials behaved, to a good approximation, according to predictions based on calculations for the ideal case mentioned earlier.

The leachates from the columns containing organic matter were variable in respect to pH and calcium concentration (Table 2). With Soil No. 3, the pH of the leachate was 9.30 compared with 8.30 and 7.19 for the suspensions at the low and high $P_{CO_2}$'s respectively. The calcium concentrations corresponding to these pH values were $0.22\times10^{-3}$, $1.53\times10^{-3}$ and $4.40\times10^{-3}$ respectively. The leachate from Peat (a) had a pH of 8.20 and a calcium concentration of $0.45\times10^{-3}$M. This sample of peat when obtained from the field was extremely acid and, therefore, in its natural state did not exist in a calcareous medium under leaching conditions. Furthermore, at the end of 48 hours the pH of the leachate was still increasing slowly. It seemed obvious that over a long period of time the pH of the leachate would become much higher. This conclusion is based on the fact that peat has an appreciable buffering capacity above neutrality (3). The solution of $CaCO_3$ in the absence of $CO_2$ from external sources tends to cause an increase in pH. Organic matter, however, by reacting to reduce the hydroxyl ion concentration allows more $CaCO_3$ to dissolve and thereby increases the $P_{CO_2}$ of the solution. Titrating with a solution of $Ca(OH)_2$ should, therefore, cause the same final result as continuous leaching. Consequently, after 48 hours' leaching with water, 300 ml. of a saturated solution of $Ca(OH)_2$ was leached through the column. After this the column was leached with water until there was no measurable change in the pH of the leachate over a period of 24 hours (material

designated as Peat (b) in the tables). The pH and calcium concentration of the leachate at this time were 9.2 and $0.18\times10^{-3}$M respectively. The suspensions made in the usual way had pH values of 8.20 and 7.11 at the low and high $P_{CO_2}$'s respectively, and the corresponding calcium concentrations were $1.86\times10^{-3}$ and $6.10\times10^{-3}$M. These values for Peat (b) are similar to those obtained with Soil No. 3. Soil No. 4 as obtained from the field had a pH of 8.09 at a $P_{CO_2}$ of $4\times10^{-4}$ atm. and showed no exchange acidity at pH 7. However, since it contained little if any solid $CaCO_3$, some was added before placing the soil in the column. After 48 hours' leaching the pH of the leachate was still increasing measurably with time. The leaching was continued for 10 days, after which the pH did not change measurably over a 24-hour period. The pH and calcium concentration of the leachate at this time were 8.80 and $0.25\times10^{-3}$M respectively. The pH values of the suspensions were 8.44 and 7.22 with $P_{CO_2}$'s of $3\times10^{-4}$ and $5\times10^{-2}$ atm. respectively and the corresponding calcium concentrations were $1.27\times10^{-3}$ and $5.10\times10^{-3}$M.

It was calculated that a calcium concentration of $10^{-3}$M from salts other than $CaCO_3$ should cause a decrease in the pH of the leachate of about 0.3 of a pH unit. Three columns, one each of sand, kaolin and vermiculite, prepared as described in Table 1, were leached with $10^{-3}$M $CaCl_2$ in place of water. The pH of the leachates varied from 9.30 to 9.50, compared with 9.80 when water was the leaching solution.

## DISCUSSION

The most striking feature concerning the results presented above was that, when water was leached through a column of non-organic calcareous materials, regardless of the exchange capacity of the material, the pH of the leachate was always near 9.8 with a calcium concentration of roughly $0.13\times10^{-3}$M, whereas when the calcareous material contained organic matter the pH of the leachate varied considerably. Length of time of leaching was of much more importance when organic matter was present than with the non-organic materials. In fact, although in most of the experiments the recorded measurements were made after leaching for 48 hours, there was very little change in the constitution of the leachates from the non-organic materials after about 4 hours. There seems little doubt that, with the columns containing organic matter, the variation in pH of the leachates was caused by the relatively high buffering capacity of organic matter on the alkaline side of neutrality.

The very significant differences between the pH and calcium concentrations of the leachates and the corresponding values for the suspensions suggest that the pH of a soil-water suspension exposed to the air may be quite different from the actual pH in a calcareous soil under leaching conditions. The very pronounced effect of organic matter on the constitution of the leachates demonstrates, however, that it is not possible to predict from calculations based on an ideal model what the pH or calcium concentration of the leachates will be.

Although many more experiments could have been made concerning the effect of organic matter on the pH of the leachates, it was felt that such results would be strictly empirical in nature until much more is known of the structure of soil organic matter. Any further work along this line, for the time being at least, should probably be restricted to actual soil profiles.

## REFERENCES

1. Cole, C. N. Hydrogen and calcium relationships of calcareous soils. Soil Sci. 83: 141-150. 1957.
2. Ericksson, E. The physico-chemical behaviour of nutrient in soils. J. Soil Sci. 3: 238-250. 1952.
3. Feustel, I. C. The acidic properties of peat and muck. U.S. Dept. Agr. Tech. Bull. 690. 1939.
4. Turner, R. C., and J. S. Clark. The pH of calcareous soils. Soil Sci. 82:337-341. 1956.
5. Turner, R. C. A theoretical treatment of the pH of calcareous soils. Soil Sci. (*In Press*).
6. Yaalon, D. H. Physico-chemical relationships of $CaCO_3$, pH and $CO_2$ in calcareous soils. Trans. 5th Intern. Congr. Soil Sci. II:356-363. 1954.

# A SELF-RECORDING SOIL PENETROMETER[1]

A. L. MATHIEU AND J. A. TOOGOOD[2]

*University of Alberta, Edmonton, Alberta*

[Received for publication July 8, 1957

## ABSTRACT

A new model of a recording penetrometer to measure soil compaction and consistency is described. It differs from previous penetrometers in its controlled rate and depth of probe penetration and in the ease with which replications can be made. It has been developed for field use to enable many recorded readings to be taken conveniently in a short time.

## INTRODUCTION

The measurement of the physical properties of soils *in situ* is one of the major problems in soil science at the present time. One of the methods to measure variations in soil consistency and compaction involves the use of a penetrometer, a probe forced downwards into the soil. This has been done by impact (6); at a constant rate by a crank (1, 3, 5); by an electrically-driven mechanism (2); or by means of a manual push (4, 7). Some of the penetrometers are light in weight (4, 7); others are heavy (1, 3) and, even when mounted on wheels (2, 5), are not manoeuvrable in the field. The recording mechanism on the penetrometers may incorporate a drum (1, 3, 5) or a flat chart (2, 4, 7). These require lined sheets which must be changed after each measurement is completed, and this is not too convenient under field conditions. A controlled rate of probe penetration is essential, and while this feature is achieved in the crank-driven penetrometers (1, 5), much time is required to remove the probe from the ground. The depth of probe penetration is limited by the length of the probe-stem and the degree of soil compaction. This presents a problem in the penetrometers mentioned if the sub-soil characteristics are to be investigated. The main difficulty in using penetrometers has been the need for extensive and speedy replications due to the great variability of successive readings.

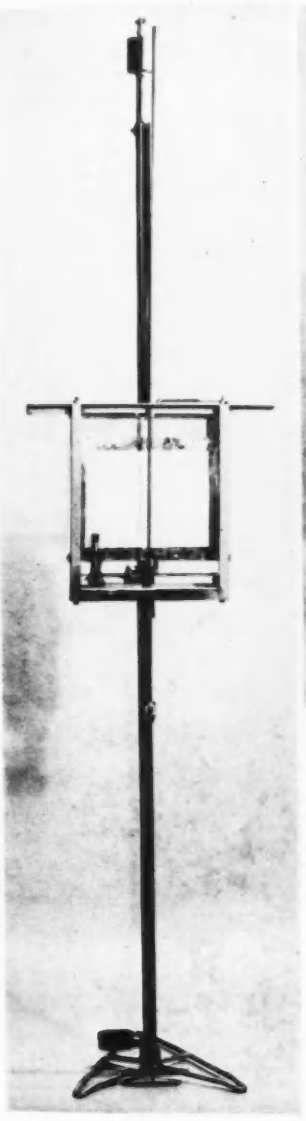
## DESCRIPTION OF PENETROMETER

The penetrometer consists of three systems: 1) to measure the pressure applied on the probe; 2) to regulate the vertical rate of probe movement; and 3) to record the pressure and probe depth. Figure 1 shows an over-all view of the penetrometer. Details of its construction are available from the senior author and only a few general remarks will be made here concerning the three main parts and their operation.

The main components of the pressure-measuring system are a probe and probe-stem which are linked to two calibrated compression springs by a T-frame. In this respect, this penetrometer resembles certain earlier models (3, 4). Probes of varying sizes and shapes can be attached to the probe-stem so that a wide range of soil conditions may be studied using the

[1] Contribution from the University of Alberta, Department of Soil Science, and the Research Council of Alberta, Edmonton, Alta.

[2] Graduate student and Associate Professor, respectively.



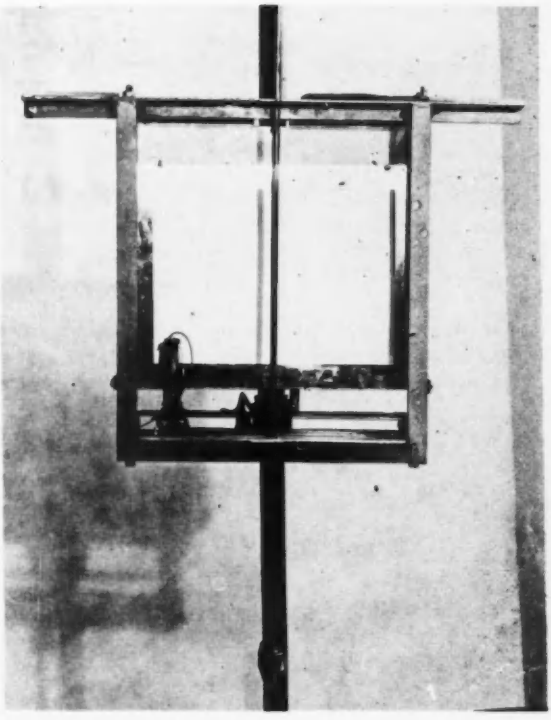


FIGURE 2. Close-up view of the recording mechanism of the penetrometer. Note pulleys, cord, pen and pen-carriage.

FIGURE 1 (left). Front view of penetrometer ready for use in the field. Total height may be reduced to about 4 feet for transportation.

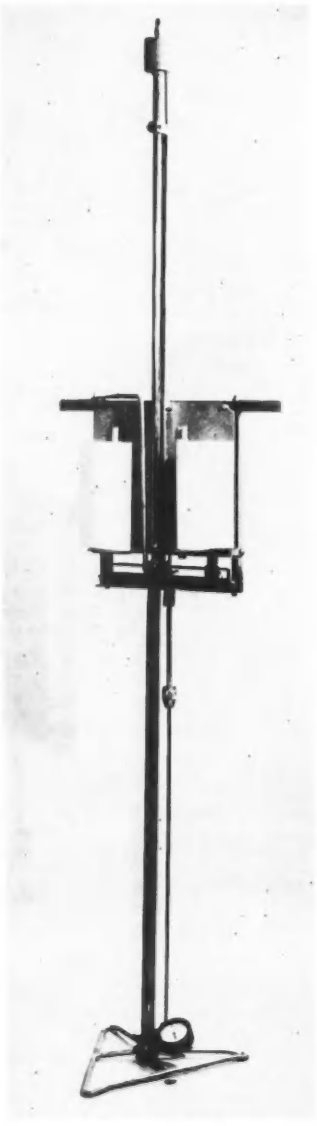


FIGURE 3. Rear view of the penetrometer, showing blank paper roll on the spools. Observe oil pressure gauge and oil reservoir at top.

same set of compression springs. A continuous probe-stem permits probe penetration to a depth of 6 feet in 2-foot increments, if needed, by adjusting a tension screw. A stop collar on the tongue of the T-frame limits vertical movement and compression of the springs. Thus, until stopped by the collar, the pressure-measuring system is free floating and responsive to pressure required to overcome the resistance of soil to probe penetration.

The system utilized for controlling the vertical rate of probe movement is a feature of this penetrometer. It consists essentially of an hydraulic system with a pressure gauge attached and a piston through which the fluid passes by way of a small orifice as the probe is pushed downward. By keeping the pressure in the hydraulic chamber constant, a steady rate of descent of the probe is assured. The probe can be quickly lifted out of the soil, since a release valve permits the fluid to flow back to the hydraulic chamber.

The recording system (Figure 2) consists of a self-filling pen attached to a small guided carriage on the horizontal part of the T-frame and a roll of blank paper. The roll of paper is threaded camera-wise on the two

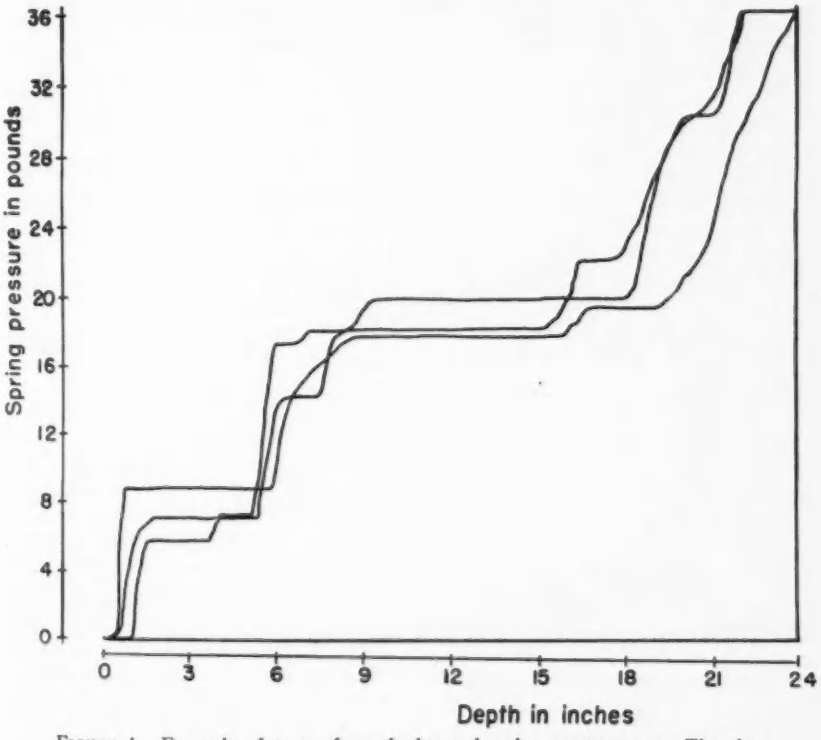



FIGURE 4. Example of type of graph drawn by the penetrometer. The three curves are replications within a one-foot circle. The vertical lines on the graph represent relative degrees of compacted layers encountered by the probe at various depths in the soil.

spools at the back of the chart frame so that the paper is exposed at the front and can be quickly altered to a new position (Figure 3). The carriage can travel a maximum of 8 inches. A cord and three pulleys convert the vertical movements of the probe to horizontal movements of the pen carriage in the ratio of 3:1, 2:1, or 1:1, as desired. The resistance encountered by the probe as it is forced into the soil is indicated by the movement of the pen in a vertical direction.

A replicated penetrometer reading taken in the field is shown in Figure 4. The pen draws the pressure-depth function line as the probe is forced downward; when the tension on the springs is released, the pen draws the "Y" axis. The "X" axis is drawn as the probe is pulled out of the ground as the pen returns to its starting position by means of a spring and cord. Since no adjustments are necessary between readings, the operator may immediately begin a replication. Readings can be taken rapidly—80-100 per hour is an average number—and the paper roll can accommodate the readings of as many as 150 replicated locations. A specially constructed viewing frame makes reference and study of the roll of readings simple.

This instrument has been used for the past 5 years and has proven very satisfactory under field conditions.

## REFERENCES

1. Culpin, C. Studies on the relation between cultivation implements, soil structure and the crop. J. Agr. Sci. 26:22-35. 1936.
2. Reed, I. F. A method of studying soil packing by tractors. Agr. Eng. 21:281-282. 1940.
3. Richards, S. J. A soil penetrometer. Soil Sci. Soc. Amer. Proc. 6:104-107. 1941.
4. Robertson, L. S., and C. M. Hansen. A recording soil penetrometer. Mich. Agr. Expt. Sta. Quart. Bull. 33:1-4. 1950.
5. Shaw, B. T., R. H. Haise, and R. B. Farnsworth. Four years experience with a soil penetrometer. Soil Sci. Soc. Amer. Proc. 7:48-55. 1942.
6. Stone, A. A., and I. L. Williams. Measurement of soil hardness. Agr. Eng. 20:25-26. 1939.
7. Terry, C. W., and H. M. Wilson. The Cornell soil penetrometer. Agr. Eng. 33:425. 1952.

# HALOMORPHISM OF SOME CLAY SOILS IN MANITOBA[1]

W. A. EHRLICH[2] AND R. E. SMITH[3]

*Winnipeg, Manitoba*

[Received for publication May 5, 1958]

## ABSTRACT

The analysis of the principal horizons of 11 halomorphic profiles was undertaken in an attempt to ascertain, chiefly, the kind and quantity of soluble salts and exchangeable cations assumed to be the main causative agents in the formation of solonetzic soils in Manitoba. The results showed that water-soluble sodium was equal to or greater in quantity than water-soluble calcium or water-soluble magnesium; that exchangeable calcium followed closely by exchangeable magnesium dominated the exchange complexes; and that exchangeable sodium in excess of 15 per cent of the exchangeable cations was found only in some horizons of the Solonchak, Solonetz and Solodized-Solonetz soils in the Chesterfield Association.

## INTRODUCTION

Soils that reflect the effect of soluble salts have been widely studied by soil scientists concerned with their classification and nomenclature. Notwithstanding the widespread investigations and extensive literature published on these soils, there are divergent views, particularly on soils with solonetzic morphology, as to whether they should be defined by morphological or by chemical characteristics. In general, the controversy has revolved around the relative influence of exchangeable magnesium compared to that of exchangeable sodium on the formation of soils with solonetzic morphology.

De Sigmond (7) defined a Solonetz as a soil containing a minimum of 12 per cent exchangeable sodium in the complex. He stated that the term solonetz, when applied to a soil containing a dominance of exchangeable magnesium, refers only to the structure of the soil. Kellogg (10) and many others have concurred with the statements made by de Sigmond.

A minority group of investigators, consisting of Bentley and Rost (2), Rost and Maehl (16), Ellis and Caldwell (4) and a few others, maintain that high quantities of exchangeable magnesium, accompanied by low quantities of exchangeable sodium, occur in some soils with solonetzic morphology. Explanation for the high magnesium and low sodium content in the exchange complex, by Joffe (8) and other proponents of the sodium theory, was secondary salinization. This explanation, in effect, implied that the Solonetz and Solodized-Solonetz soils were formed under the influence of sodium which was later replaced mainly by magnesium.

The object of this paper is to present the results of a series of analyses dealing principally with soluble salts and exchangeable cations occurring in catenary groups containing soils with the morphological characteristics of Solonchak, Solonetz and Solodized-Solonetz.

---

[1] Contribution from Department of Soils, University of Manitoba, Winnipeg, Man.
[2] Research Officer, Experimental Farms Service, Winnipeg, Man.
[3] Agriculturist, Manitoba Department of Agriculture, Winnipeg, Man.

## MATERIALS

The eleven soils used in this study were the Solonchak, Solonetz* and Solodized-Solonetz* in the Red River, Oliver and Chesterfield associations, and the Solonetz and Solodized-Solonetz in the Gretna Association. The soils in the Red River association were sampled in Latitude N. 49° 45′ Longitude W. 97° 32′, the Gretna association in Latitude N. 49° 6′ Longitude W. 97° 30′, the Oliver Association in Latitude N. 49° 30′ Longitude W. 99° 4′ and the Chesterfield Association Latitude N. 49° 5′ Longitude W. 100° 57′. All soils were from the Black soil region. The depth of profile samplings, which ranged from 8 to 18 feet, was determined by the uniformity of the underlying materials. Generalized descriptions of the three groups of genetic profiles used in the study are given below:

### Generalized Description of the Solonchak Profiles

*$A_1$ Horizon* — Dark grey to black clay (4 to 17 inches thick); fine granular; hard; moderately alkaline; weakly calcareous and gypsiferous.

*C Horizon* — Variable in colour; clay texture; massive structure; carbonates and gypsum present in variable quantities for a depth of 42 inches in the Oliver to 14 feet in the Red River group.

*D Horizon* — Occurs in the Oliver profile at 42 inches; clay loam texture; less saline and less calcareous than material above.

### Generalized Description of the Black Solonetz Profiles

*$A_1$ Horizon* — Dark grey to very dark grey clay (2 to 5 inches thick); medium granular to sub-angular blocky; very hard; neutral to moderately alkaline; carbonates are low to absent.

*$B_2$ Horizon* — Dark grey to very dark grey clay (4 to 9 inches thick); medium prismatic; extremely hard; mildly to moderately alkaline; carbonates are low.

*$B_3$ Horizon* — Dark grey to very dark brown clay (4 to 6 inches thick); weakly developed prismatic structure; very hard; moderately alkaline; contains carbonates and some gypsum.

*C Horizon* — Variable in colour; clay texture; massive structure; carbonates and gypsum present in variable quantities for a depth of 28 inches in the Oliver to 14 feet in the Red River group.

*D Horizon* — Occurs in the Oliver profile at 28 inches; sandy loam to clay loam texture; as saline and calcareous as material above.

### Generalized Description of the Black Solodized-Solonetz Profiles

*$A_1$ Horizon* — Dark grey to very dark grey clay loam to clay (1 to 2 inches thick); fine to medium granular; slightly hard to hard; slightly acid to mildly alkaline; carbonates are very low to absent.

*$A_2$ Horizon* — Grey to light brownish grey sandy loam to clay (1 to 2 inches thick); weakly platy to fine granular; slightly hard to hard; slightly acid to mildly alkaline; carbonates are very low to absent.

*$B_1$ Horizon* — Dark grey to very dark greyish brown clay (2 to 5 inches thick); round-topped columnar structure with tops grey in color; very hard; slightly acid to neutral, carbonates are absent.

*$B_2$ Horizon* — Very dark grey to black clay (5 to 10 inches thick); columnar; extremely hard; slightly acid; carbonates are absent.

*$B_3$ Horizon* — Very dark greyish brown to black clay (4 to 27 inches thick); massive to weak columnar; very hard; neutral to moderately alkaline; carbonates and gypsum are low to absent.

*C Horizon* — Variable in colour; clay texture; massive; carbonates and gypsum present in variable quantities for a depth of 36 inches in the Oliver to 18 feet in the Red River group.

*D Horizon* — Occurs in the Oliver profile at 36 inches; clay loam texture; saline and calcareous as material above.

* In this paper the terms "Solonetz" and "Solodized-Solonetz" apply to the morphology.

## METHODS

The analyses included mechanical analysis, inorganic carbon, organic carbon, pH values, conductivity, soluble salts, exchangeable cations and exchange capacity.

The methods are outlined as follows:

*Mechanical Analysis*

The pipette method as described by Kilmer and Alexander (11) was followed with minor variations. Hydrogen peroxide was used as the digesting agent for the removal of organic matter, and sodium carbonate was used as the dispersing agent for the mineral fractions.

*Inorganic Carbon*

Inorganic carbon was determined by decomposition of the carbonates using hydrochloric acid and absorbing the resultant carbon dioxide evolved in ascarite.

*Organic Carbon*

Organic carbon was estimated by subtracting inorganic carbon from total carbon. The latter was obtained by a wet combustion method which is a modification of the ones given by Adams (1) and Waynick (18).

*pH Values*

Air-dry samples were moistened with water to a paste consistency near the lower liquid limit and the pH was determined with a Coleman glass electrode apparatus.

*Conductivity*

Conductivity was determined by the saturated soil extract method (1:1), as outlined by Hayward *et al.* (5).

*Soluble Salts*

Saturation extracts (1:1) were used for the determination of calcium, magnesium, sodium, potassium, sulphates, chlorides, bicarbonates and water-soluble carbonates.

Calcium was precipitated as calcium oxalate. This precipitate was filtered, washed, dissolved in 0.1N sulphuric acid and titrated against 0.1N potassium permanganate. The filtrate obtained from the calcium determination was precipitated with sodium ammonium phosphate as magnesium ammonium phosphate. After dissolving in 0.1N sulphuric acid the solution was titrated against sodium hydroxide containing brom cresol green indicator. Sodium and potassium were determined with a Beckman DU flame photometer. Sulphates were determined gravimetrically by precipitation with barium chloride. The analysis for carbonates and bicarbonates was carried out on the same aliquots of the extracts by a method outlined by Hayward *et al.* (5).

*Exchangeable Cations*

Exchangeable metal cations were extracted by the ammonium acetate method of Schollenberger as outlined by Kelley (9). Calcium and magnesium were determined by Jackson's (6) method. Sodium and potassium

were determined on 0.2N hydrochloric acid extracts prepared from the calcium filtrates using the Beckman DU flame photometer. Exchangeable hydrogen was extracted with barium acetate (adjusted to pH 7.0) and titrated against 0.1N sodium hydroxide using phenolphthalein as indicator.

*Exchange Capacity*

The ammonium acetate method as proposed by Atkinson* was used for this determination. The extract obtained from the leaching process was distilled and the ammonia displaced was measured by titration against 0.1N sodium hydroxide.

## RESULTS AND DISCUSSION

*Mechanical Analysis*

Examination of the mechanical analysis data of the various soils in Tables 1*a* and 1*b* indicate the following: First, there is a lack of homogeneity in clay content of all soils except in those of the Red River soil group; second, illuvial clay is slight in the B horizons of the Solenetz soils; and third, illuvial clay is pronounced in the B horizons of the Solodized-Solonetz soils.

* Atkinson, H. J., *et al.* Determination of exchange capacity. Chem. Div., Science Service, Ottawa. 1956. (*Personal communication*).

TABLE 1*a*—MECHANICAL ANALYSIS, CALCIUM CARBONATE[1], ORGANIC CARBON AND pH VALUES (IN PER CENT OF OVEN-DRY WEIGHT)

| Soil | Horizon[2] | Depth, inches | Sand 2.0–0.05 mm. | Silt 0.05–0.002 mm. | Clay <0.002 mm. | $CaCO_3$ | Organic carbon | pH |
|---|---|---|---|---|---|---|---|---|
| Red River Association Solonchak | A | 0–4 | 4.9 | 25.0 | 70.1 | 5.2 | 2.8 | 7.8 |
| | $C_{11}$ | 4–7 | 4.0 | 23.2 | 72.8 | 5.7 | 1.2 | 7.7 |
| | $C_{12}$ | 7–22 | 2.8 | 25.3 | 71.9 | 10.6 | .1 | 7.9 |
| | $C_2$ | 22–48 | 1.1 | 22.3 | 76.6 | 10.1 | .1 | 7.9 |
| | $C_2$ | 96–130 | .9 | 22.7 | 76.4 | 9.0 | .3 | 7.6 |
| | $C_2$ | 150–168 | .2 | 25.4 | 74.4 | 8.0 | .4 | 7.7 |
| Solonetz | $A_1$ | 0–5 | 9.6 | 29.7 | 60.7 | .5 | 4.8 | 6.3 |
| | $B_2$ | 5–14 | 5.1 | 21.5 | 73.4 | .1 | 1.3 | 6.1 |
| | $B_3$ | 14–18 | 2.2 | 18.2 | 79.6 | 2.9 | .4 | 7.7 |
| | $C_1$ | 18–30 | 2.0 | 19.6 | 78.4 | 10.4 | .1 | 7.9 |
| | $C_2$ | 30–48 | 1.4 | 19.6 | 80.0 | 11.9 | .2 | 7.9 |
| | $C_2$ | 84–120 | 1.5 | 27.3 | 71.2 | 11.5 | .2 | 7.6 |
| | $C_2$ | 144–168 | 3.7 | 32.0 | 64.3 | 14.5 | .1 | 7.6 |
| Solodized-Solonetz | $A_1$ | 0–2 | 10.7 | 34.1 | 51.2 | .2 | 6.4 | 5.9 |
| | $A_2$ | 2–4 | 6.3 | 25.9 | 67.8 | — | 2.5 | 5.6 |
| | $B_2$ | 8–13 | 3.7 | 18.4 | 77.9 | — | 1.3 | 5.3 |
| | $B_3$ | 18–23 | 1.9 | 20.5 | 77.6 | 1.9 | .9 | 7.5 |
| | $C_1$ | 68–74 | 1.2 | 23.5 | 75.3 | 10.5 | .3 | 7.4 |
| | $C_2$ | 98–128 | 1.7 | 38.6 | 59.7 | 12.6 | .3 | 7.3 |
| | $C_2$ | 200–224 | 4.9 | 49.2 | 45.9 | 11.3 | .3 | 7.3 |
| Gretna Association Solonetz | $A_1$ | 0–3 | 9.7 | 41.8 | 48.5 | .8 | 5.3 | 6.6 |
| | $B_2$ | 3–9 | 3.5 | 36.2 | 60.3 | .5 | 3.1 | 6.7 |
| | $B_3$ | 9–15 | 1.4 | 26.5 | 72.1 | 6.0 | 1.2 | 7.9 |
| | $C_1$ | 15–28 | 2.3 | 32.3 | 65.4 | 11.7 | .6 | 7.9 |
| | $C_2$ | 28–38 | 6.5 | 51.8 | 42.7 | 8.3 | .3 | 8.0 |
| | $C_2$ | 38–72 | 11.2 | 41.6 | 47.2 | 9.5 | .2 | 8.1 |
| | $C_2$ | 120–156 | 10.5 | 60.6 | 28.9 | 19.9 | .3 | 7.9 |
| Solodized-Solonetz | $A_1$ | 0–2 | 15.1 | 45.7 | 39.2 | .3 | 6.9 | 6.1 |
| | $A_2$ | 2–3 | 8.4 | 49.3 | 42.3 | .2 | 6.5 | 6.4 |
| | $B_2$ | 3–9 | 3.5 | 35.3 | 61.2 | .5 | 3.7 | 7.3 |
| | $B_3$ | 15–36 | 1.1 | 41.5 | 57.4 | 5.9 | .7 | 7.7 |
| | $C_2$ | 48–72 | 1.5 | 46.2 | 52.3 | 8.3 | .4 | 8.1 |
| | $C_2$ | 132–168 | 9.5 | 55.8 | 34.7 | 19.9 | .3 | 7.8 |

[1] Inorganic carbon converted to calcium carbonate.
[2] In this and subsequent Tables, some horizons were omitted for the sake of brevity.

Lack of uniformity in clay content of various soils is notable among the Gretna, Oliver and Chesterfield soil groups. This stratification of variable clay content is common to shallow-bedded lacustral areas and should not be confused with pedogenic processes. Unless illuvial clay is present in considerable amounts it is often difficult to verify its presence or absence without microscopic examination. In the case of the B horizons of the Solonetz and Solodized-Solonetz soils, it was observed that the aggregates were coated with "clay skins".

*Inorganic Carbonates*

The figures in Tables 1*a* and 1*b* showing the carbonates (expressed as $CaCO_3$ equivalent) indicate that the parent materials of the Red River, Gretna and Oliver soil associations have 8 to 20 per cent lime carbonate and the Chesterfield association has 0.1 to 5.2 per cent.

The relative concentrations of lime carbonate is one of the important criteria used in soil classification and also is an important factor in the development of soil profiles under saline or non-saline conditions. It was indicated by Ehrlich *et al.* (3) that the thickness of the sola of well-drained soils developed under similar environmental conditions varied inversely with lime carbonate content. This restrictive tendency of lime carbonate

TABLE 1*b*.—MECHANICAL ANALYSIS, CALCIUM CARBONATE, ORGANIC CARBON AND pH VALUES (IN PER CENT OF OVEN-DRY WEIGHT)

| Soil | Horizon | Depth[1], inches | Sand 2.0–0.05 mm. | Silt 0.05–0.002 mm. | Clay <0.002 mm. | $CaCO_3$ | Organic carbon | pH |
|---|---|---|---|---|---|---|---|---|
| Oliver Association Solonchak | $A_{11}$ | 0–8 | 4.9 | 49.2 | 45.9 | 1.9 | 2.9 | 7.8 |
| | $A_{12}$ | 8–17 | 15.1 | 45.5 | 39.4 | 1.7 | 2.0 | 8.1 |
| | $C_1$ | 17–26 | 11.7 | 39.3 | 49.0 | 4.9 | .6 | 8.1 |
| | $C_2$ | 26–42 | 8.7 | 41.4 | 49.9 | 12.7 | .2 | 8.1 |
| | D | 42–60 | 21.1 | 44.3 | 34.6 | 17.2 | — | 7.7 |
| | D | 60–84 | 18.8 | 55.8 | 25.4 | 17.0 | — | 7.7 |
| Solonetz | A | 0–3 | 2.6 | 58.4 | 39.0 | .9 | 7.1 | 7.4 |
| | $B_2$ | 7–12 | 7.5 | 39.9 | 52.6 | .1 | 1.5 | 7.2 |
| | $C_2$ | 22–28 | 3.7 | 38.0 | 58.3 | 1.0 | .7 | 7.7 |
| | D | 36–48 | 42.7 | 32.7 | 24.6 | 13.7 | .6 | 7.7 |
| | D | 60–84 | 27.0 | 58.9 | 14.1 | 17.9 | 1.0 | 7.8 |
| Solodized-Solonetz | $A_1$ | 0–2 | 7.6 | 68.6 | 23.8 | .5 | 10.5 | 7.3 |
| | $A_2$ | 2–4 | 13.6 | 61.2 | 25.2 | — | 2.7 | 7.2 |
| | $B_1$ | 4–8 | 5.7 | 39.9 | 54.4 | — | 1.2 | 6.9 |
| | $B_2$ | 8–14 | 4.9 | 32.6 | 62.5 | — | 1.2 | 6.8 |
| | $C_2$ | 26–36 | 2.6 | 34.0 | 63.4 | 9.5 | .8 | 7.5 |
| | D | 48–60 | 16.8 | 54.5 | 28.7 | 11.1 | .5 | 7.6 |
| Chesterfield Association Solonchak | A | 0–6 | 6.5 | 43.4 | 50.1 | .9 | 3.0 | 7.8 |
| | $C_1$ | 6–12 | 2.4 | 63.9 | 33.7 | 2.1 | 1.3 | 7.9 |
| | $C_2$ | 12–24 | 2.1 | 31.5 | 66.4 | 2.5 | .7 | 7.9 |
| | $C_2$ | 48–60 | 1.7 | 40.8 | 57.5 | 2.5 | .7 | 8.1 |
| | $C_2$ | 72–96 | 4.2 | 53.2 | 42.6 | 1.6 | .1 | 8.2 |
| Solonetz | A | 0–2 | 9.2 | 42.4 | 48.4 | .1 | 4.7 | 6.7 |
| | $B_2$ | 2–9 | 9.6 | 26.0 | 64.4 | .1 | 2.1 | 7.5 |
| | $B_2$ | 9–14 | 8.3 | 36.7 | 55.0 | 2.6 | 1.0 | 8.1 |
| | $C_1$ | 25–36 | 12.9 | 32.8 | 54.3 | 4.2 | .1 | 8.1 |
| | $C_2$ | 96–106 | 12.1 | 45.9 | 42.0 | 5.2 | — | 8.0 |
| Solodized-Solonetz | $A_1$ | 0–1.5 | 21.2 | 58.6 | 20.2 | — | 2.9 | 5.9 |
| | $A_2$ | 1.5–3 | 20.1 | 62.1 | 17.8 | — | 2.0 | 6.1 |
| | $B_1$ | 8–13 | 3.7 | 41.0 | 55.3 | — | 1.0 | 6.8 |
| | $B_2$ | 18–26 | 2.3 | 41.8 | 55.9 | .9 | .4 | 7.4 |
| | $C_1$ | 36–48 | 9.1 | 69.7 | 21.2 | 1.4 | .1 | 7.7 |
| | $C_2$ | 60–72 | 4.3 | 57.2 | 38.5 | .1 | .4 | 6.0 |

[1] In subsequent Tables, the depth is omitted for the sake of brevity.

TABLE 2*a*.—CONDUCTIVITY AND SOLUBLE SALTS (MOISTURE-FREE BASIS)

| Soil | Horizon | Conductivity (mmhos/cm.) | Cations (per cent) | | | | Anions (per cent) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | Na | K | $SO_4$ | Cl | $HCO_3$ | $CO_3$ |
| Red River Association | | | | | | | | | | |
| Solonchak | A | 1.0 | .011 | .003 | .002 | .001 | .025 | .001 | .030 | — |
| | $C_{11}$ | 3.9 | .051 | .017 | .010 | .002 | .266 | .002 | .012 | — |
| | $C_{12}$ | 6.7 | .042 | .045 | .041 | .002 | .502 | .005 | .008 | — |
| | $C_2$ | 6.0 | .032 | .033 | .050 | .002 | .417 | .009 | .010 | — |
| | $C_2$ | 5.6 | .048 | .024 | .041 | .003 | .379 | .012 | .009 | — |
| | $C_2$ | 4.5 | .051 | .020 | .045 | .004 | .281 | .018 | .012 | — |
| Solonetz | $A_1$ | .9 | .008 | .003 | .004 | .002 | — | .003 | .037 | — |
| | $B_2$ | .6 | .004 | .002 | .004 | .001 | .002 | .004 | .017 | — |
| | $B_3$ | 1.1 | .008 | .005 | .016 | .001 | .010 | .016 | .030 | — |
| | $C_1$ | 1.8 | .010 | .006 | .031 | .001 | .043 | .034 | .002 | — |
| | $C_2$ | 3.0 | .018 | .010 | .046 | .001 | .095 | .060 | .016 | — |
| | $C_2$ | 6.0 | .069 | .032 | .046 | .004 | .340 | .076 | .014 | — |
| | $C_2$ | 5.5 | .053 | .029 | .045 | .004 | .272 | .055 | .010 | — |
| Solodized-Solonetz | $A_1$ | 1.0 | .013 | .007 | .003 | .002 | .001 | .006 | .048 | — |
| | $A_2$ | .4 | .005 | .002 | .002 | .001 | .003 | .002 | .016 | — |
| | $B_2$ | .4 | .004 | .003 | .004 | .001 | .015 | .006 | .007 | — |
| | $B_3$ | 1.5 | .013 | .008 | .013 | .001 | .018 | .031 | .018 | — |
| | $C_1$ | 7.0 | .075 | .043 | .042 | .004 | .235 | .141 | .009 | — |
| | $C_2$ | 7.7 | .075 | .040 | .056 | .005 | .198 | .176 | .009 | — |
| | $C_2$ | 5.8 | .058 | .024 | .047 | .004 | .123 | .133 | .009 | — |
| Gretna Association | | | | | | | | | | |
| Solonetz | $A_1$ | 1.0 | .011 | .003 | .004 | .003 | .004 | .002 | .044 | — |
| | $B_2$ | .6 | .003 | .002 | .006 | .001 | .001 | .004 | .020 | — |
| | $B_3$ | .9 | .007 | .003 | .008 | .001 | .004 | .005 | .029 | — |
| | $C_1$ | 4.7 | .051 | .015 | .053 | .001 | .325 | .002 | .016 | — |
| | $C_2$ | 7.9 | .047 | .022 | .173 | .001 | .548 | .003 | .011 | — |
| | $C_2$ | 10.4 | .046 | .028 | .246 | .002 | .704 | .016 | .010 | — |
| | $C_2$ | 8.7 | .045 | .025 | .188 | .002 | .550 | .031 | .008 | — |
| Solodized-Solonetz | $A_1$ | .9 | .006 | .002 | .010 | .002 | — | .006 | .044 | — |
| | $A_2$ | 1.0 | .003 | .001 | .018 | .002 | .004 | .009 | .042 | — |
| | $B_2$ | 4.0 | .009 | .006 | .080 | .002 | .126 | .035 | .057 | — |
| | $B_3$ | 13.5 | .057 | .051 | .287 | .003 | .790 | .104 | .022 | — |
| | $C_2$ | 11.2 | .055 | .042 | .239 | .003 | .685 | .081 | .012 | — |
| | $C_2$ | 8.7 | .046 | .027 | .157 | .002 | .554 | .030 | .013 | — |

to profile development is more strongly emphasized in the poorly drained soils because of the additional lime carbonate supplied by run-off and ground waters. Under both saline and non-saline conditions, the presence of an abundance of lime carbonate not only restricts profile development through the precipitating effects of the released calcium and magnesium but also serves as a supply of alkaline earth cations for the adsorption complex. Since the replacing power of calcium and magnesium is considerably greater that that of sodium it is evident that the presence of appreciable quantities of lime carbonate would result in a proportionally high adsorption of the alkaline earth cations on the complex. The relative high magnesium adsorption on the soil complexes is in part attributable to the abundant supply of magnesium in the primary limestone rock occurring in the Red River Valley in Manitoba.

*Organic Carbon*

Data on organic carbon in Tables 1*a* and 1*b* point out two features of interest: First, percentage organic carbon in the $A_1$ horizons increases (with the exceptions of the Solodized-Solonetz in the Chesterfield soil group) from the Solonchak to the Solodized-Solonetz; and second, translocation of organic colloids from the A to the B horizons in the solonetzic soils appears to be slight.

TABLE 2*b*.—CONDUCTIVITY AND SOLUBLE SALTS (MOISTURE-FREE BASIS)

| Soil | Horizon | Conductivity (mmhos/cm.) | Cations (per cent) | | | | Anions (per cent) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | Na | K | $SO_4$ | Cl | $HCO_3$ | $CO_3$ |
| Oliver Association Solonchak | $A_{11}$ | 15.0 | .058 | .082 | .265 | .004 | 1.008 | .033 | .045 | — |
| | $A_{12}$ | 13.8 | .047 | .065 | .264 | .002 | .934 | .012 | .024 | — |
| | $C_1$ | 11.0 | .043 | .045 | .210 | .002 | .727 | .005 | .013 | — |
| | $C_2$ | 8.2 | .041 | .033 | .139 | .001 | .522 | .002 | .012 | — |
| | D | 4.9 | .048 | .028 | .060 | .002 | .319 | .002 | .013 | — |
| | D | 3.0 | .020 | .018 | .038 | .002 | .158 | .002 | .022 | — |
| Solonetz | $A_1$ | 1.4 | .015 | .008 | .010 | .003 | .027 | .005 | .058 | — |
| | $B_2$ | 2.1 | .019 | .009 | .023 | .002 | .083 | .006 | .037 | — |
| | $C_2$ | 4.7 | .051 | .030 | .035 | .001 | .302 | .003 | .017 | — |
| | D | 3.7 | .048 | .019 | .029 | .001 | .223 | .003 | .012 | — |
| | D | 3.9 | .049 | .024 | .026 | .002 | .243 | .002 | .010 | — |
| Solodized-Solonetz | $A_1$ | 1.4 | .013 | .006 | .003 | .003 | .005 | .006 | .081 | — |
| | $A_2$ | .5 | .011 | .003 | .003 | .002 | .001 | .002 | .031 | — |
| | $B_1$ | .6 | .014 | .004 | .003 | .002 | .020 | .006 | .037 | — |
| | $B_2$ | .7 | .009 | .004 | .008 | .001 | .043 | .002 | .018 | — |
| | $C_2$ | 2.8 | .024 | .015 | .032 | .001 | .161 | .007 | .020 | — |
| | D | 2.0 | .025 | .013 | .028 | .001 | .128 | .006 | .017 | — |
| Chesterfield Association Solonchak | $A_1$ | 6.3 | .017 | .009 | .135 | .001 | .330 | .005 | .042 | .001 |
| | $C_1$ | 18.0 | .049 | .022 | .491 | .002 | 1.211 | .004 | .023 | — |
| | $C_2$ | 18.6 | .047 | .050 | .465 | .004 | 1.266 | .005 | .021 | — |
| | $C_2$ | 18.0 | .084 | .117 | .392 | .004 | 1.472 | .005 | .019 | — |
| | $C_2$ | 19.6 | .044 | .101 | .448 | .004 | 1.433 | .004 | .019 | — |
| Solonetz | $A_1$ | 2.4 | .023 | .008 | .033 | .002 | .043 | .006 | .076 | .002 |
| | $B_2$ | 2.2 | .013 | .007 | .037 | .001 | .061 | .007 | .062 | — |
| | $B_3$ | 9.1 | .046 | .055 | .154 | .001 | .624 | .004 | .042 | — |
| | $C_1$ | 10.8 | .045 | .069 | .186 | .001 | .761 | .004 | .012 | — |
| | $C_2$ | 8.6 | .049 | .029 | .145 | .002 | .536 | .004 | .009 | — |
| Solodized-Solonetz | $A_1$ | 1.1 | .012 | .002 | .012 | .007 | .004 | .004 | .052 | — |
| | $A_2$ | .7 | .010 | .002 | .012 | .002 | .010 | .003 | .024 | — |
| | $B_2$ | .4 | .011 | .002 | .003 | .001 | .020 | .001 | .024 | — |
| | $B_3$ | 3.4 | .061 | .016 | .017 | .002 | .212 | .001 | .026 | — |
| | $C_1$ | 8.6 | .048 | .041 | .142 | .002 | .582 | .002 | .014 | — |
| | $C_2$ | 4.5 | .013 | .007 | .079 | .001 | .237 | .002 | .004 | — |

The increase of organic matter in the $A_1$ horizons of soils in the process of desalinization is obviously due to a more favourable soil media for plant growth. Less favourable soil media for plant growth, and consequently lower organic matter content, may be encountered in solonetzic soils with higher percentages of exchangeable sodium. Movement of organic colloids from the A to B horizons in the Solonetz and Solodized-Solonetz soils, which is not evident in the data, is, however, indicated on the soil aggregates in the B horizons.

*pH Values*

The pH values in the sola of the various groups of soils range from moderately alkaline in the Solonchak to slightly or moderately acid in the Solodized-Solonetz soils. (See Tables 1*a* and 1*b*). From this data it is apparent that the sodium hydroxide at present formed is insignificant; otherwise higher reactions would have been recorded, particularly in the Solonetz soils.

## CONDUCTIVITY AND SOLUBLE SALTS

The conductivity and soluble salt measurements shown in Tables 2*a* and 2*b* correspond reasonably well with one another except where an abundance of chloride salts is indicated. In samples with appreciable quantities

TABLE 3*a*.—EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY (MOISTURE-FREE BASIS)

| Soil | Horizon | Per cent of total cations | | | | | Exchange[1] capacity |
|---|---|---|---|---|---|---|---|
| | | Ca | Mg | Na | K | H | |
| Red River Association | A | 65.4 | 32.9 | .4 | 1.3 | — | 50.1 |
| Solonchak | $C_{11}$ | 63.2 | 35.3 | .5 | 1.0 | — | 43.3 |
| | $C_{12}$ | 45.3 | 53.6 | .4 | .7 | — | 37.1 |
| | $C_2$ | 40.9 | 57.9 | .4 | .7 | — | 35.5 |
| | $C_2$ | — | — | .5 | .7 | — | 35.3 |
| | $C_2$ | — | — | .6 | .8 | — | 37.4 |
| Solonetz | $A_1$ | 56.9 | 34.0 | .2 | 2.0 | 6.9 | 46.0 |
| | $B_2$ | 49.7 | 43.0 | .9 | 1.1 | 5.3 | 49.1 |
| | $B_2$ | 52.2 | 46.2 | .8 | .8 | — | 46.7 |
| | $C_1$ | 51.8 | 46.8 | .6 | .8 | — | 43.3 |
| | $C_2$ | 51.1 | 48.1 | .2 | .6 | — | 41.2 |
| | $C_2$ | — | — | .1 | .5 | — | 34.3 |
| | $C_2$ | — | — | .2 | .4 | — | 31.9 |
| Solodized-Solonetz | $A_1$ | 56.2 | 30.2 | .5 | 1.4 | 11.7 | 55.9 |
| | $A_2$ | 47.1 | 37.9 | 1.7 | 1.8 | 11.5 | 49.3 |
| | $B_2$ | 45.9 | 41.9 | .9 | 1.6 | 9.7 | 54.7 |
| | $B_2$ | 51.6 | 45.8 | 1.2 | 1.4 | — | 45.3 |
| | $C_1$ | — | — | .3 | 1.2 | — | 34.4 |
| | $C_2$ | — | — | .3 | 1.7 | — | 33.1 |
| | $C_2$ | — | — | .3 | 1.7 | — | 32.7 |
| Gretna Association | $A_1$ | 62.2 | 30.4 | .2 | 2.6 | 4.6 | 45.3 |
| Solonetz | $B_2$ | 45.3 | 49.3 | 1.3 | 1.7 | 2.4 | 45.1 |
| | $B_2$ | 50.2 | 47.1 | 1.8 | .9 | — | 43.9 |
| | $C_1$ | — | — | 1.1 | 1.5 | — | 35.2 |
| | $C_2$ | — | — | 3.0 | 1.2 | — | 33.1 |
| | $C_2$ | — | — | 4.4 | 1.4 | — | 26.9 |
| | $C_2$ | — | — | — | 1.6 | — | 18.5 |
| Solodized-Solonetz | $A_1$ | 58.9 | 26.7 | 1.6 | 2.4 | 10.4 | 38.8 |
| | $A_2$ | 53.9 | 31.9 | 3.6 | 2.3 | 8.3 | 37.7 |
| | $B_2$ | 36.2 | 53.1 | 6.5 | 3.5 | .7 | 44.7 |
| | $B_2$ | — | — | 8.6 | 2.1 | — | 37.0 |
| | $C_2$ | — | — | .6 | 1.2 | — | 32.3 |
| | $C_2$ | — | — | — | 2.0 | — | 19.6 |

[1] Milli-equivalents per 100 grams of oven-dry soil

of chlorides, the conductivity measurements are higher than in samples with similar quantities of sulphates. The effect of chlorides on conductivity is indicated in the Solodized-Solonetz soil of the Red River Association.

Conductivity measurements greater than 4 millimhos/cm. are noted in one or more horizons of all profiles except in the Solodized-Solonetz soil of the Oliver Association. The Oliver group of soils has a coarser-textured substratum than the other groups and in consequence much more effective leaching of salts has occurred during the desalinization stage. Decreasing amounts of soluble salts in the sola for the respective stages of solonization and solodization also are evident in the other soil groups.

The data reveal that the composition and quantity of salts vary from one group of soils to the other. Sulphates, in general, dominate the anions in all soils. Chlorides, however, are high in the $C_2$ horizon of the Solodized-Solonetz in the Red River group. Bicarbonates are relatively high in the surface horizons of all solonized and solodized soils. Water-soluble carbonates occur only in trace amounts in the A horizons of the Solonetz and Solodized-Solonetz soils of the Chesterfield group.

Variation in the quantity of water-soluble calcium and magnesium salts from one group to another is comparatively small. From the Solonchak to the Solodized-Solonetz a progressive lowering in concentration of these salts in the sola under sustained leaching effects is fairly uniform among the different soil groups. Water-soluble calcium, in general, is dominant over magnesium and in the Red River soils is greater in quantity than water-

TABLE 3*b*.—EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY (MOISTURE-FREE BASIS)

| Soil | Horizon | Per cent of total cations | | | | | Exchange[1] capacity |
|---|---|---|---|---|---|---|---|
| | | Ca | Mg | Na | K | H | |
| Oliver Association | $A_{11}$ | 44.8 | 48.2 | 5.9 | 1.1 | — | 39.0 |
| Solonchak | $A_{12}$ | 55.0 | 42.3 | 1.7 | 1.0 | — | 33.3 |
| | $C_1$ | | | 7.8 | 1.6 | — | 30.9 |
| | $C_2$ | | | 11.4 | 1.8 | — | 28.0 |
| | D | | | 5.1 | 1.0 | — | 19.5 |
| | D | | | 6.2 | 1.8 | — | 16.1 |
| Solonetz | $A_1$ | 70.4 | 25.0 | .7 | 3.3 | .6 | 36.2 |
| | $B_2$ | 59.8 | 35.9 | 1.5 | 1.7 | 1.1 | 44.6 |
| | $C_1$ | | | 1.0 | 1.0 | — | 30.2 |
| | D | | | 2.5 | 1.5 | — | 20.4 |
| | D | | | .9 | 1.9 | — | 3.5 |
| Solodized-Solonetz | $A_1$ | 69.1 | 26.3 | .3 | 2.8 | 1.5 | 3[illegible] |
| | $A_2$ | 71.5 | 21.9 | .8 | 2.9 | 2.9 | [illegible] |
| | $B_1$ | 56.9 | 37.5 | .9 | 2.4 | 2.3 | .1 |
| | $B_2$ | 48.0 | 47.0 | 1.4 | 2.3 | 1.3 | 47.2 |
| | $C_2$ | | | 1.1 | .8 | — | 35.4 |
| | D | | | 2.6 | 1.6 | — | 15.5 |
| Chesterfield Association | $A_1$ | 35.7 | 30.8 | 30.2 | 2.3 | — | 40.8 |
| Solonchak | $C_1$ | | | 7.3 | 2.5 | — | 39.7 |
| | $C_2$ | | | 19.4 | 2.5 | — | 36.6 |
| | $C_2$ | | | 19.1 | 2.5 | — | 36.1 |
| | $C_2$ | | | 8.1 | 2.6 | — | 34.5 |
| Solonetz | $A_1$ | 53.1 | 39.0 | 1.4 | 1.8 | 4.7 | 45.4 |
| | $B_2$ | 42.9 | 49.3 | 5.8 | 1.5 | .5 | 50.5 |
| | $B_2$ | 46.1 | 48.4 | 4.7 | .8 | — | 47.8 |
| | $C_2$ | | | 17.7 | 1.2 | — | 40.6 |
| | $C_2$ | | | 9.6 | 1.2 | — | 38.5 |
| Solodized-Solonetz | $A_1$ | 49.3 | 26.7 | 1.9 | 3.8 | 18.3 | 31.0 |
| | $A_2$ | 36.1 | 32.4 | — | 3.9 | 27.6 | 15.4 |
| | $B_2$ | 46.2 | 46.3 | 2.7 | 2.0 | 2.8 | 36.3 |
| | $B_2$ | | | .3 | 1.8 | — | 39.2 |
| | $C_1$ | | | 2.9 | 1.7 | — | 34.3 |
| | $C_2$ | | | 17.0 | 1.6 | — | 34.1 |

[1] Milli-equivalents per 100 grams of oven-dry soil

soluble sodium. In the other soil groups, water-soluble sodium exceeds the other cations except in some horizons of the Solonetz and Solodized-Solonetz soils in the Oliver group.

It is apparent from the analysis that water-soluble sodium is one of the principal constituents in the salinization stage in the Red River, Gretna, Oliver and Chesterfield associations. Sodium content in relation to calcium or magnesium content increases progressively from the Red River group to the Chesterfield group, that is, from east to west.

Proportionally greater sodium concentration is indicated in Saskatchewan soils by Mitchell (13) and in Alberta soils by MacGregor and Wyatt (12). Southward along the Red River Valley in Minnesota, Rost and Chang (15) report results which correspond favourably with the salt analysis of soils for the Red River Valley in Manitoba.

The narrow ratio of sodium to magnesium in some salinized soils in the Red River Valley has been reported for soils in other regions. In soils such as these it is understandable that sodium will not play a prominent role in the development of solonetzic soils because of the high solubility of its salts and the comparatively high replacing power of the divalent cations. These aspects are indicated in the data. It would appear that the ratio of sodium to magnesium or calcium must be wide before appreciable quantities of sodium are adsorbed by the complex.

## EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

Exchangeable calcium in general is dominant over the other cations in all soils. Exchangeable magnesium exceeds sodium and is greater than calcium in the C horizon of the Solonchak in the Red River group, in the $B_2$ horizon of the Solonetz and Solodized-Solonetz in the Gretna group, in the $A_{11}$ of the Solonchak in the Oliver group and in the $B_2$ of the Solonetz and Solodized-Solonetz in the Chesterfield group. Exchangeable-sodium percentage of 15 specified by Hayward *et al.* (5) as the minimum for saline-alkali and non-saline alkali soils is reached only in a few horizons of the Solonchak, Solonetz and Solodized-Solonetz soils in the Chesterfield group. The Solonized and Solodized soils in the latter group probably would not qualify for the names applied, in that the percentage exchangeable sodium specified occurs below the sola. Exchangeable potassium is low but fairly uniform in content in all soils. Exchangeable hydrogen is found in the sola of the Solonetz and Solodized-Solonetz soils.

Exchange capacity for the various soils is high and is indicative not only of the clay content of the different horizons but also of the kind of clay. According to Ehrlich *et al.* (3) the clay minerals in Manitoba are predominantly montmorillonite followed by smaller quantities of illite.

In view of the evidence on soluble salts and exchangeable cations in these soils it can be assumed that the quantity of water-soluble sodium must be much greater in quantity than calcium or magnesium before appreciable exchange of sodium for the divalent cations occurs in the complex. From the data given it is apparent that exchangeable sodium does not approach the minimum of 15 per cent specified by Hayward *et al.* (5) in the sola of the Solonetz and Solodized-Solonetz soils. It is possible, although unlikely, that a high percentage of exchangeable sodium existed on each complex in the early stages of desalinization and was replaced by the divalent cations before the Solonetz soil was developed. This possibility, however, is extremely unlikely in the Red River group which had comparatively low concentrations of water-soluble sodium compounds in the saline stage. In view of the identical morphological features of these soils to other soils reported with 15 per cent or more of exchangeable sodium in the complexes, it appears that the high quantity of sodium specified does not apply under all conditions to the development of solonetzic soils. This premise is given in support of the researches of Rost and Maehl (16), Ellis and Caldwell (4), Riecken (14), Kelley (9) and several others. These workers indicate that exchangeable magnesium can be the main contributing factor in the formation of solonetzic soils low in exchangeable-alkali cations.

From the data presented in this paper it appears that exchangeable magnesium, rather than exchangeable sodium, was the main dispersing agent. Further examination of the data reveals that solonetzic soils can develop in the presence of fairly high calcium saturation. In these soils, the exchangeable calcium and exchangeable magnesium ratio is narrow and only in a few horizons of the solonetzic soils is calcium exceeded by magnesium in content. Frantzesson, quoted by Kelley (9), states that "certain solonetz soils of Russia are characterized by high calcium saturation". It appears, therefore, that soils with solonetzic morphology are not always associated with a particular base status of the exchange material.

The genesis and classification of soils with solonetzic morphology are at present in a state of confusion. In essence, the confusion is due to the connotative naming by the early investigators of these soils on the basis of both composition and morphology. Since most of the original solonetzic soils investigated had an appreciable content of exchangeable sodium, it was assumed that this cation was the sole criterion. Gedroiz, quoted from Kelley (9), asserts that "the word 'Solonetz' refers simply to high percentage sodium saturation" and this soil is "usually characterized by a peculiar type of morphology". The majority of workers concur with Gedroiz and do not accept the theory of exchangeable magnesium under any conditions as being one of the contributing cations in the formation of soils with solonetzic morphology. Since the magnesium theory is supported by a number of investigators it appears, therefore, that the Russian terms in use should be discarded and new terms used to apply to the morphology. It is impossible for field-men to distinguish by visual means the difference between soils high in exchangeable sodium and in exchangeable magnesium.

## ACKNOWLEDGEMENTS

Acknowledgements are due to L. E. Pratt, Experimental Farms Service; and to E. A. Poyser and F. P. Leclaire, Manitoba Department of Agriculture, for their assistance in sampling of soils and for analytical determinations.

## REFERENCES

1. Adams, J. E. Determination of total carbon in soils by wet combustion method. Ind. Eng. Chem., Anal. Ed. 6:227. 1934.
2. Bentley, C. F., and C. O. Rost. A study of some solonetzic soil complexes in Saskatchewan. Sci. Agr. 27:293–313. 1947.
3. Ehrlich, W. A., H. M. Rice, and J. H. Ellis. Influence of the composition of parent materials on soil formation in Manitoba. Can. J. Agr. Sci. 35:407-421. 1955.
4. Ellis, J. H., and O. G. Caldwell. Magnesium clay solonetz. Trans. 3rd Intern. Congr. Soil Sci. 1:348-350. 1935.
5. Hayward, H. E., *et al.* Diagnosis and improvement of saline and alkali soils. U.S. Regional Salinity Lab. Agr. Handb. 60. U.S. Dept. Agr., Washington, D.C. 1954.
6. Jackson, M. L. Soil analysis: Chemical and physical methods. Manual of methods. Mimeographed. Madison, Wis. 1946-1949.
7. Janzen, W. R., and H. C. Moss. Exchangeable cations in Solodized-Solonetz and solonetz-like soils in Saskatchewan. J. Soil Sci. 7:203-212. 1956.
8. Joffe, Jacob, S. Pedology. Pedology Publications, New Brunswick, N.J. 1949.
9. Kelley, W. P. Cation exchange in soils. Reinhold Publ. Corp., New York, N.Y. 1948.
10. Kellogg, C. E. Morphology and genesis of Solonetz soils of western North Dakota. Soil Sci. 38:483–501. 1934.
11. Kilmer, V. J., and L. T. Alexander. Methods of making mechanical analysis in soils. Soil Sci. 68:15-24. 1949.
12. MacGregor, J. M., and F. A. Wyatt. Solonetz soils of Alberta. Soil Sci. 59:419-435. 1945.
13. Mitchell, J. Alkali soils in Saskatchewan. Sci. Agr. 18:120-125. 1937.
14. Riecken, F. F. Some considerations in the magnesium cycle of weathering of Solonetz. Soil Sci. Soc. Amer. Proc. 8:391–395. 1943.
15. Rost, C. O., and P. C. Chang. Exchangeable bases of Solonchak of the Red River Valley. Soil Sci. Soc. Amer. Proc. 6:354-359. 1941.
16. Rost, C. O., and K. A. Maehl. Some solodized soils of the Red River Valley. Soil Sci. 55:301-312. 1943.
17. Sigmond, A. A. J. de. Principles of soil science. Thomas Murby and Co., London, England. 1938.
18. Waynick, D. D. A simplified wet combustion method for the determination of carbon in soils. Ind. Eng. Chem. 11:634. 1919.

# RATE OF CHANGE OF pH IN SOME ACID SOILS DUE TO LIMING[1]

K. F. NIELSEN[2]

[Received for publication November 8, 1957]


## ABSTRACT

Lime at the rate of 0, 3000, 6000, 12,000 and 24,000 pp2m was applied to four acid soils and allowed to incubate for a period of 140 days. The rate and extent of change in pH was followed.

In all four soils the rate of reaction was very rapid and most of the increase in pH was obtained within 3 days after application. At all rates of liming in the four soils there was a general decrease in pH following the peak obtained within the first 30 days.

It was also found that the rate of change in pH of a soil that had been limed was greatly influenced by the moisture content. The change in pH was much more rapid and extensive at 25 per cent moisture than at 10 per cent.


## INTRODUCTION

A knowledge of how rapidly the pH of an acid soil will change when lime is applied is important, since much of the agriculturally valuable land in the world is acid in reaction and requires lime to bring it into best productivity.

There are many factors which will influence the rate of change in pH. Important among these are: original pH, exchange capacity, per cent base saturation, texture, moisture content, fineness of the lime, total neutralizing power and degree of mixing in the soil.

Soils with high exchange capacities are more highly buffered than those with low capacities and, therefore, possess more potential acidity at any particular pH value. The change in pH of a soil that has been limed will, therefore, be materially influenced by the degree of base saturation (1). A relationship has been shown to exist between pH value and exchangeable acidity in soils, and indeed forms the basis for estimating the lime requirement in some procedures. Both $H^+$ ions and $Al^{+++}$ ions are effective in causing acidity in soils.

Finely ground lime will dissolve into solution more rapidly than coarsely ground lime and, the better the mixing, the more rapidly the lime dissolves.

Present methods of evaluating the amount of lime required to correct the acidity of a soil give little or no information as to how rapidly the desired pH will be attained.

This article is a report of a laboratory study in which the rate of change in pH of four acid soils was evaluated using different rates of lime application. Included also are data concerning the influence of moisture content on the pH of a soil.

## MATERIALS AND METHODS

Four soils were used in this study: Bangor silt loam, Caribou loam, Hermon sandy loam, and Merrimac sandy loam. These soils are characterized in Table 1.

[1] Most of the work reported was done at the University of Maine, Orono, Maine

[2] Field Husbandry Division, Central Experimental Farm, Ottawa, Ontario

TABLE 1.—CHARACTERIZATION OF SOILS

| Soil type | Exchange capacity m.e. per 100 gm. | Exchangeable bases m.e. per 100 gm. | Organic matter % | pH |
|---|---|---|---|---|
| Bangor silt loam | 10.51 | 0.90 | 4.40 | 5.40 |
| Caribou loam | 17.60 | 1.80 | 6.18 | 5.30 |
| Hermon sandy loam | 11.06 | 3.25 | 6.60 | 6.00 |
| Merrimac sandy loam | 9.21 | 0.70 | 4.20 | 5.20 |

The limestone used was Rockland Rockport commercial lime. It analysed 33.31 per cent CaO and 17.82 per cent MgO and was ground so that it would all pass a 100-mesh screen.

In the part of the experiment where all four soils were used, 750 gm. lots were treated with lime at rates of 0, 3000, 6000, 12,000 and 24,000 parts per 2 million, (equivalent to pounds per acre) and mixed well. Water was added in amounts to bring the soils to approximately field capacity, mixed into the soil, and the soil then placed in quart cans. The water content was maintained thereafter at a point somewhat less than field capacity. The treatments were replicated three times.

The soils were sampled for pH measurement immediately after the lime and water had been incorporated. The values obtained are shown in Figures 1-4 as the initial pH. The pH measurements were taken every 24 hours for the first week, every 3 days for the next 2 weeks, and every week thereafter for a total of 140 days.

Where the influence of water on rate and extent of reaction was studied, 500 gm. of soil were placed in pint containers. The covers were loosely sealed, so that carbon dioxide would not build up sufficiently to influence the pH (3). About 3 gm. of water evaporated from each in a week's time. Three lime treatments of 0, 3000, and 6000 parts per 2 million, and two water rates, 10 per cent and 25 per cent by weight, were used. The soils were made up to weight each week and thoroughly mixed. The pH measurements were made every 24 hours for the first week and every week thereafter for a total of 38 days. At the end of this time the soils were allowed to dry out. The soils that had been wetted to 25 per cent previously were then wetted to 10 per cent, and vice versa. The pH change was followed in the same way as previously for a period of 63 days.

The soil was wetted to a paste and a Beckman pH meter employing a glass electrode was used for making the pH measurements.

The pH measurements were taken on the soil directly from the containers. The samples were not dried first. They were wetted up and read within 15 minutes.

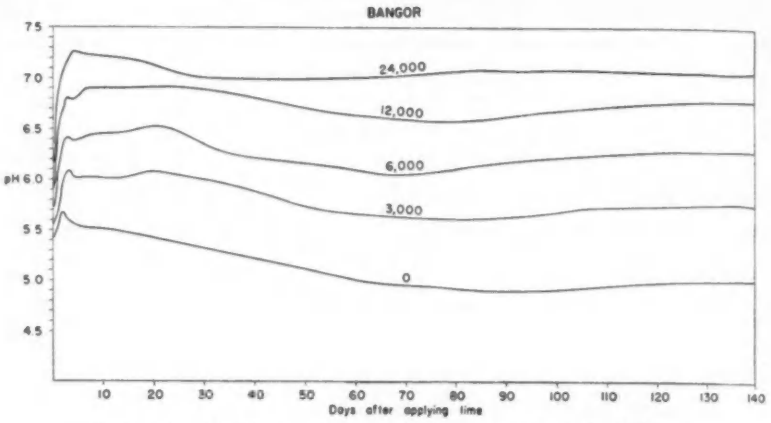



FIGURE 1. pH Change in Bangor silt loam when treated with lime.

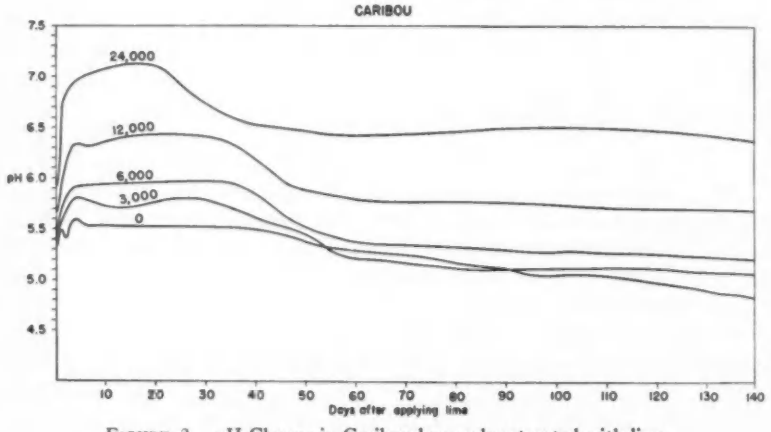



FIGURE 2. pH Change in Caribou loam when treated with lime.

## RESULTS AND DISCUSSION

*Effect of Rate of Lime Application on pH*

The pH changes in the four soils as affected by different quantities of lime are shown in Figures 1-4.

These figures show that the initial change in pH of all the soils was rapid, most of the increase occurring within 3 days of the application of the lime, and essentially all of it within 30 days.

From the peak in pH obtained at all rates of liming there was a general decrease and levelling-off. The decrease was greatest with the Caribou loam, and least with the Merrimac sandy loam. The Hermon and Bangor soils were intermediate. This is the general order of the exchange capacity values for these soils.

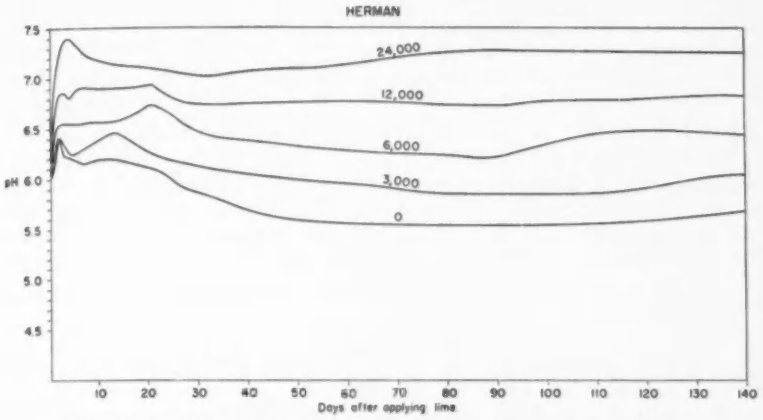



FIGURE 3. pH Change in Hermon sandy loam when treated with lime.

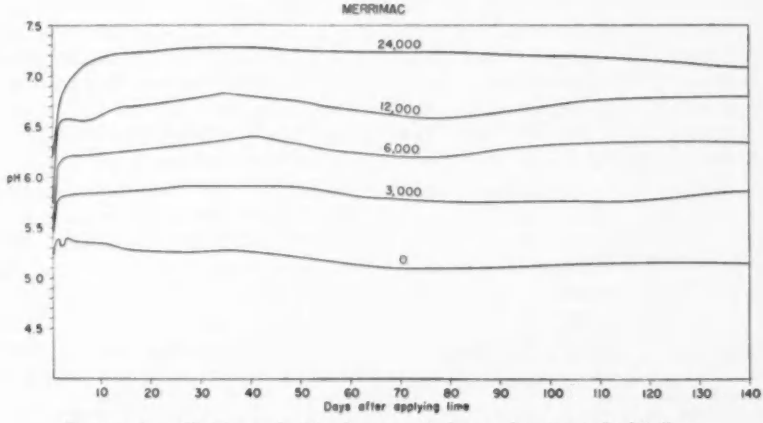



FIGURE 4. pH Change in Merrimac sandy loam when treated with lime.

The buffering capacity of these soils is demonstrated in that the 24,000 parts per 2 million rate did not cause the pH to rise any more than about 1.8 units, even in the sandy Merrimac loam. In the Caribou loam, the final pH with this heavy application dropped back to a point only one unit above the original level. The highest rate of lime maintained the pH above the neutral point in all soils except the Caribou loam.

Figures 1-4 show that the final pH of the untreated soils was invariably lower than the initial pH and in the case of Caribou loam, the most pronounced, was a full half-unit lower. The final readings of these untreated soils may have been closer to the actual pH of these soils under field conditions than the initial. This effect may be of importance where pH determinations are made on farmers' samples since the samples are first air-dried, then wetted and allowed to equilibrate for only a short time.

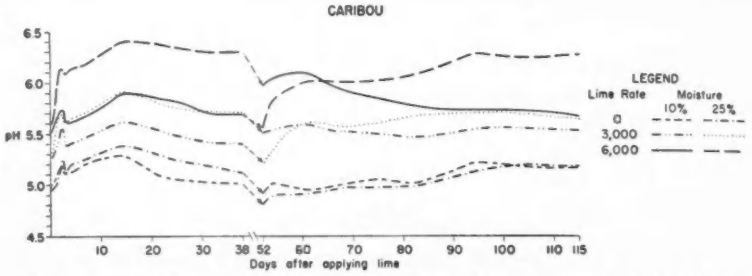



FIGURE 5. pH Change in Caribou loam treated with lime when held at different moisture percentages.

When one considers what takes place when lime is added to a moist soil, the following steps may be recorded:

1. The surface molecules on the lime particles pass into solution, with the result that the solution and soil immediately adjacent to the particles may become saturated with respect to $CaCO_3$.

During this process hydrogen and aluminium ions on the exchange complex of the soil are replaced by calcium ions and go into the soil solution. Ordinarily this would cause a reduction in the pH of the solution, since pH is approximated by log $[H^+]$ but, because of the quantity of $CO_3^{--}$ ions (from the lime) and $OH^-$ ions (from the water), the net effect is usually an increase in pH, since the acid $H_2CO_3$ is weaker than the base $Ca(OH)_2$.

2. As the $Ca^{++}$ ions diffuse into Ca-unsaturated areas, they replace other $H^+$ and $Al^{+++}$ ions from the exchange complex of the soil. As the $Ca^{++}$ ions disappear from the solution, the effective concentration of $OH^-$ ions is decreased, causing a drop in pH. The larger the exchange capacity, the larger the reduction in pH that could be expected.

It is suggested that a combination of these two effects, plus those which cause a change in the unlimed samples (whether they were the same or different is not known), could have caused the shape of the curves in Figures 1-4.

*Effect of Soil Moisture on pH*

The effects of soil moisture on rate of pH change and level of pH in a Caribou loam soil treated with different quantities of lime are shown in Figure 5.

The higher soil moisture percentage of 25 almost invariably resulted in a more rapid and extensive change in pH than did the 10 per cent.

The curve for the first period of 3000 parts per 2 million lime under 25 per cent moisture was almost identical to that of the 6000 parts per 2 million rate at 10 per cent moisture for the same period. However, when the former sample was changed to 10 per cent moisture and the latter to 25 per cent, there was a marked difference in the curves.

Considering the same rates again, the curve for the second period (52-115 days after applying lime) for the 6000 parts per 2 million rate which had been reduced to 10 per cent from 25 per cent moisture became nearly

identical to that of the curve for the 3000 parts per 2 million rate which had been increased to 25 per cent from 10 per cent moisture. The curves for the zero treatment were different for the first period but nearly the same for the second.

The pH of a soil in the field is not a constant value. It has been shown to vary during the growing season (2). Moisture is undoubtedly important in causing this variation. As the moisture is removed from a given sample of soil, the salt concentration in the solution surrounding the exchange complexes of the soil becomes greater. This will result in a replacement of $H^+$ and $Al^{+++}$ ions on the complex by the mineral cations, causing a reduction in the pH of the solution.

## REFERENCES

1. Mehlich, A. Base unsaturation and pH in relation to soil type. Soil Sci. Soc. Amer. Proc. 6:150-156. 1942.
2. Swanback, T. R., and M. F. Morgan. Seasonal fluctuations in soil reaction. Conn. Agr. Expt. Sta. Bull. 311, pp. 264-268. 1930.
3. Whitney, R. S., and R. Gardner. The effect of carbon dioxide on soil reaction. Soil Sci. 55:127-141. 1943.

# CHEMICAL COMPOSITION OF THE PEAT BOGS OF THE MARITIME PROVINCES[1]

D. G. Smith,[2] C. Bryson,[3] E. M. Thompson[3] and E. Gordon Young[4]

*Atlantic Regional Laboratory, National Research Council, Halifax, Nova Scotia*

[Received for publication March 7, 1958]

## ABSTRACT

The proximate chemical composition of seven peat bogs in the Maritime Provinces has been determined. The results have been expressed as profiles in relation to depth and as over-all averages for each bog.

The acidity tended to be high at pH 3.9–4.8; the moisture content was 90–95 per cent; the total ash was low at 0.5–3 per cent of which about 14 per cent was CaO, 0.85 per cent $K_2O$, and 2.7 per cent $P_2O_5$. Of the organic constituents the fraction containing waxes and resins averaged about 7 per cent of the dry matter in most bogs. The total nitrogen was less than 1 per cent. Hemicelluloses and other substances soluble in hot dilute HCl constituted 32–42 per cent of the dry matter and humic substances 28–34 per cent.

The process of humification was indicated by a decrease in cellulose, hemicelluloses and gums, and an increase in humic substances, waxes and resins.

## INTRODUCTION

The industry in peat moss has grown rapidly in Canada since 1940 (10). About 125,000 tons with a value of over $3,700,000 were marketed in 1956.

Since several bogs in the Maritime Provinces are under commercial development and practically no analyses have been done on the chemical composition of this peat, a systematic investigation of both inorganic and organic constituents has been carried out and is here reported briefly. Such information is essential to any chemical development of these bogs. It should contribute to a better comprehension of the chemical nature of humification and the passage of moss to peat to lignite.

The most extensive chemical analyses of peat and peat moss have been done by Risi *et al.* (7) in Quebec, by Black, Cornhill and Woodward (2) and Mitchell (5) in Scotland, by Odén and Lindberg (6) and Theander (11, 12) in Sweden and by Waksman and Stevens (14) in the United States.

## MATERIALS AND METHODS

### *Materials*

Specimens were obtained from the Caribou bog, Kings Co., Nova Scotia, from the Lameque and Shippigan bogs, Gloucester Co., New Brunswick, and from the East Bideford, Black Banks, Black Marsh, and Portage bogs, Prince Edward Island. About 100 samples were collected and analysed. All of the bogs have been surveyed by Leverin (3) and Leverin and Cameron (4). Samples were generally taken from positions across the bog, at depths of 0–2, 3–5, 8–10, 12–14, and 16–18 feet, with a modified Davis sampler. They were placed in polythene bags for transportation. The dimensions of the ordinary Davis sampler were enlarged to provide a sample of about 200 gm. The chamber was made from standard $1\frac{1}{2}''$ brass pipe and was $19\frac{1}{2}''$ long with a conical end. The extension rods were cut into 3′ lengths from $\frac{1}{2}''$ standard aluminum pipe and furnished with coupling attachments.

[1] Issued as N.R.C. No. 4869.
[2] Assistant Research Officer.
[3] Research Technician.
[4] Director.

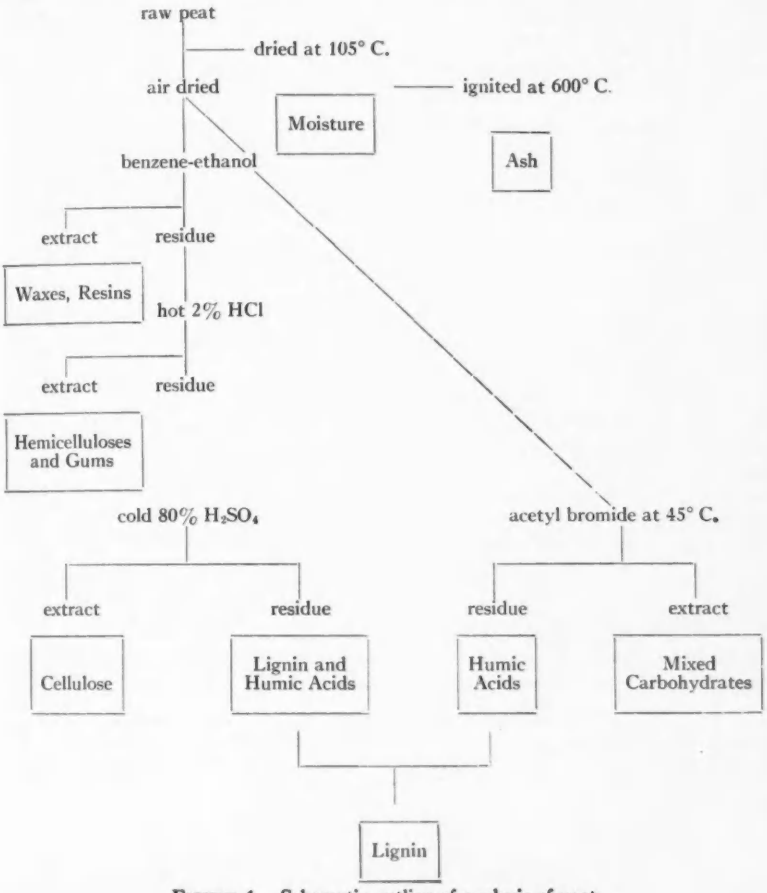



FIGURE 1. Schematic outline of analysis of peat.

The botanical composition of the bogs was not determined except for those in New Brunswick. The general composition of other bogs has been indicated by Leverin (3).

*Methods*

The scheme of analysis was patterned on that of Vermynck (13) as modified by Risi *et al.* (17)

The pH of the fresh material was measured within 0.2 unit by the direct application of "accutint" paper.

Moisture was determined by drying fresh peat in an oven at 105° C. The remainder of the sample was spread on filter paper and dried in air for 3 or 4 days at room temperature. The air-dried material was ground in a Wiley mill to pass through a 40-mesh sieve and stored in glass bottles. The moisture content of this material was then determined.

*Inorganic Constituents.* An aliquot was ignited in a muffle furnace at 600° C. to obtain the content of *total ash.* The silica in the ash was made insoluble by acidification and evaporation to dryness. The residue was moistened with conc. HCl, diluted with water to definite volume and filtered.

*Calcium* was determined on the filtrate by a microvolumetric procedure (1). *Phosphorus* was estimated colorimetrically at 700 mμ with molybdic acid (1) after ashing 1 gm. of air-dried peat with magnesium nitrate. *Potassium* and *sodium* were measured in the filtrate with a Coleman flame photometer.

*Organic Constituents.* The total organic *nitrogen* was determined by the micro-Kjeldahl method.

The *bituminous residue* was obtained by extraction of air-dried peat in a Soxhlet apparatus with a mixture of benzene and ethanol (9:1). The residue in the flask after evaporation was weighed.

The residue in the Soxhlet extraction thimble was dried at 105° C. An aliquot was boiled with 2 per cent HCl for 5 hours. The mixture was filtered with suction through a tared, coarse, sintered-glass crucible. The residue was dried at 105° C. and weighed. The filtrate and washings were neutralized with potassium hydroxide (25%) and diluted to volume. The reducing power in this solution was measured colorimetrically (8). This value multiplied by 0.9 was taken to be *hemicellulose.*

The insoluble residue after extraction of hemicelluloses was treated with 80 per cent (w/v) of $H_2SO_4$ according to Risi *et al.* (7). The reducing power was estimated as before and was taken to be *cellulose.*

*Humic substances* were determined on the air-dried material with acetylbromide (7). The mixture was filtered through a tared sintered-glass

TABLE 1.—COMPOSITION OF PEAT FROM CARIBOU BOG, NOVA SCOTIA

| | | | | As percentage of total solids | | | | | | | | | As percentage of ash | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Station | Depth (ft.) | pH | Moisture (%) | Bitumen | Hemicelluloses | Other substances sol. in HCl (2%) | Cellulose | Other substances sol. in $H_2SO_4$ (80%) | Humic acids | Lignin | Total N | Total ash | Calcium | Potassium | Phosphorus | Sodium |
| N-112 | 0–2 | 4.4 | 94.3 | 5.2 | 14.7 | 26.3 | 12.0 | 5.7 | 15.6 | 10.4 | 0.9 | 1.2 | 8.3 | 1.0 | 1.8 | 1.6 |
| | 3–5 | 4.4 | 94.0 | 7.1 | 11.6 | 22.5 | 13.7 | 6.0 | 23.3 | 15.8 | 0.9 | 0.9 | 10.4 | 0.9 | 1.1 | 2.9 |
| | 8–10 | 4.4 | 94.8 | 5.4 | 12.4 | 24.3 | 14.2 | 6.1 | 21.1 | 16.5 | 0.9 | 0.9 | 10.9 | 0.9 | 1.1 | 2.5 |
| | 12–14 | 4.6 | 93.7 | 10.7 | 8.4 | 13.2 | 9.4 | 4.7 | 39.7 | 13.9 | | 1.3 | 8.4 | 0.7 | 1.1 | 1.5 |
| | 16–18 | 4.6 | 91.3 | 11.5 | 4.9 | 8.2 | 6.2 | 3.9 | 54.3 | 10.9 | 1.2 | 1.7 | 7.5 | 0.5 | 1.2 | 1.2 |
| N-88 | 0–2 | 4.0 | 81.2 | 4.5 | 19.7 | 27.2 | 4.2 | 9.4 | 16.6 | 18.5 | 0.8 | 2.0 | 7.8 | 1.1 | 1.6 | 1.3 |
| | 3–5 | 4.0 | 93.6 | 6.4 | 17.7 | 24.5 | 6.3 | 8.5 | 22.6 | 14.1 | 0.7 | 0.6 | 12.0 | 1.4 | 2.0 | 4.5 |
| | 8–10 | 4.0 | 95.3 | 5.9 | 15.3 | 22.5 | 7.1 | 7.8 | 26.8 | 14.5 | 0.6 | 0.8 | 10.4 | 1.2 | 1.5 | 4.6 |
| | 12–14 | 4.0 | 95.2 | 7.9 | 12.4 | 17.2 | 0.6 | 7.7 | 38.9 | 15.3 | 0.6 | 0.8 | 8.3 | 1.4 | 1.6 | 3.9 |
| | 16–18 | 4.0 | 93.7 | 7.7 | 9.2 | 12.1 | 0.4 | 5.7 | 53.2 | 11.8 | 0.9 | 1.2 | 13.1 | 0.7 | 1.4 | 2.1 |
| O-72 | 0–2 | 4.0 | 88.6 | 4.8 | 15.0 | 29.7 | 10.6 | 5.7 | 18.4 | 15.8 | 0.8 | 2.8 | 6.9 | 1.6 | 1.5 | 1.3 |
| | 3–5 | 4.0 | 92.5 | 5.9 | 10.6 | 22.5 | 12.9 | 6.4 | 31.6 | 10.0 | 0.9 | 1.1 | 8.0 | 1.2 | 1.8 | 5.1 |
| | 10–12 | 4.0 | 91.8 | 9.5 | 7.6 | 12.8 | 6.2 | 4.7 | 46.3 | 12.8 | 1.0 | 1.5 | 10.0 | 0.6 | 1.4 | 1.7 |
| | 14–16 | 4.0 | 92.9 | 8.7 | 7.9 | 13.7 | 5.4 | 3.4 | 41.0 | 19.9 | 1.0 | 2.4 | 12.3 | 0.4 | 1.0 | 1.2 |
| N-32 | 0–2 | 4.0 | 92.6 | 4.0 | 21.9 | 32.8 | 1.7 | 11.5 | 13.8 | 14.2 | 0.6 | 2.4 | 3.0 | 2.1 | 1.4 | 1.5 |
| | 3–5 | 4.0 | 91.5 | 5.2 | 15.3 | 27.5 | 1.2 | 11.3 | 23.3 | 16.2 | 0.6 | 0.8 | 5.9 | 0.7 | 1.5 | 2.5 |
| | 8–10 | 4.0 | 90.0 | 14.8 | 6.3 | 8.5 | 3.1 | 3.8 | 57.4 | 6.1 | 0.7 | 1.9 | 4.5 | 0.5 | 0.9 | 1.1 |
| Av. (over-all) | | | | 7.8 | 12.0 | 20.0 | 7.6 | 6.4 | 32.1 | 14.1 | 0.9 | 1.4 | 8.4 | 1.0 | 1.5 | 2.2 |

crucible. From the amount of dry residue the *humic substances* were calculated (9). The content of *lignin* was obtained by difference. An outline of the scheme of separation is shown in Figure 1.

## RESULTS

### *Nova Scotia*

The Caribou bog contains the largest deposit of peat in Nova Scotia. Thirty-five specimens were taken from eight stations. The results of four typical borings across the bog are shown in Table 1, together with the over-all averages for all stations.

The content of material soluble in organic solvents increased with depth from about 5 per cent at the surface to about 10 per cent at the lower levels. Values for hemicellulose were highest at the surface and decreased with depth from about 15 to 6 per cent. The content of cellulose was generally at a maximum at 3 to 10 feet. The concentration of lignin was very variable with maximum values usually between 8 and 14 feet but occasionally at the surface. Values for organic nitrogen were relatively constant at 0.8 to 1.2 per cent and showed a tendency to increase somewhat with depth. Most of the organic matter was humic substances. These increased with depth from about 20 per cent at the surface to over 50 per cent at 16 to 18 feet.

Substances, other than hemicelluloses, soluble in boiling 2 per cent HCl comprised about a quarter of the material at the surface. They decreased with depth as for hemicelluloses. This fraction was probably made up of polyheteroglycans, such as gums, as distinct from pentosans, some hexosans, pectic substances and polyuronides as hemicelluloses. It would also include partial hydrolytic products of these carbohydrates and of protein. The value for residual carbohydrate, which was not cellulose, amounted to about 5 to 8 per cent and was lowest at the bottom of the bog.

TABLE 2.—COMPOSITION OF PEAT IN LAMEQUE AND SHIPPIGAN BOGS, NEW BRUNSWICK

| | | | | As per cent of total solids | | | | | | | | | As per cent of ash | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Station | Depth (ft.) | pH | Moisture (%) | Bitumen | Hemicelluloses | Other substances sol. in HCl (2%) | Cellulose | Other substances sol. in $H_2SO_4$ (80%) | Humic acids | Lignin | Total N | Total ash | Calcium | Potassium | Phosphorus | Sodium |
| L1–4 | 3–4 | 4.6 | 91.2 | 5.7 | 16.2 | 30.3 | 8.1 | 8.1 | 6.6 | 25.0 | 0.6 | 1.4 | 9.8 | 0.6 | 0.8 | 2.4 |
| | 6–7 | 4.6 | 93.8 | 4.9 | 16.1 | 26.8 | 12.6 | 5.8 | 19.1 | 14.6 | 0.5 | 1.8 | 5.0 | 0.6 | 0.6 | 1.9 |
| | 9–10 | 4.3 | 90.2 | 10.5 | 11.3 | 15.2 | 3.4 | 6.4 | 40.2 | 13.0 | 0.8 | 1.9 | 8.1 | 0.5 | 0.9 | 1.4 |
| | 12–13 | 4.8 | 87.3 | 13.9 | 4.4 | 13.8 | 0.8 | 7.8 | 32.8 | 6.0 | 0.9 | 24.1 | 0.2 | 0.8 | 0.2 | 0.2 |
| L9–13 | 3–4 | 4.6 | 95.0 | 4.2 | 20.1 | 33.8 | 11.9 | 5.2 | 12.7 | 12.0 | 0.5 | 0.9 | 7.8 | 0.8 | 1.4 | 2.9 |
| | 6–7 | 4.6 | 94.4 | 7.2 | 17.1 | 26.0 | 12.3 | 3.8 | 18.3 | 15.4 | 0.7 | 0.8 | 13.8 | 0.8 | 1.5 | 3.8 |
| | 9–10 | 4.6 | 94.1 | 4.5 | 17.7 | 31.0 | 15.3 | 3.5 | 12.0 | 16.0 | 0.3 | 0.6 | 21.8 | 0.6 | 1.3 | 3.1 |
| | 12–13 | 4.6 | 95.1 | 5.9 | 16.0 | 29.6 | 13.5 | 3.9 | 22.0 | 9.0 | 0.5 | 1.1 | 22.1 | 0.2 | 1.1 | 0.5 |
| | 15–16 | 4.4 | 92.7 | 10.8 | 10.4 | 14.7 | 4.6 | 4.6 | 37.2 | 17.7 | 0.9 | 2.9 | 15.3 | 0.2 | 0.7 | 0.3 |
| S1–2 | 3–4 | 4.3 | 91.1 | 8.4 | 12.4 | 18.0 | 5.6 | 5.6 | 42.0 | 7.9 | 1.0 | 1.2 | 8.2 | 0.9 | 1.9 | 2.6 |
| | 6–7 | 4.6 | 91.9 | 5.3 | 16.4 | 29.7 | 4.6 | 9.2 | 22.2 | 12.5 | 0.6 | 0.7 | 8.4 | 0.8 | 1.8 | 5.2 |
| S4–5 | 3–4 | 4.6 | 90.9 | 6.7 | 14.9 | 28.3 | 10.4 | 6.3 | 16.5 | 17.0 | 0.8 | 0.7 | 10.5 | 0.6 | 1.9 | 4.5 |
| | 6–7 | 4.6 | 91.2 | 7.7 | 12.9 | 15.7 | 6.3 | 6.5 | 44.4 | 6.5 | 0.7 | 0.9 | 10.2 | 1.8 | 1.8 | 3.2 |
| Av. | Lameque | | | 7.4 | 14.3 | 23.6 | 8.0 | 5.6 | 25.0 | 13.6 | 0.6 | 1.5 | 13.5 | 0.5 | 1.0 | 1.9 |
| | Shippigan | | | 7.0 | 14.2 | 22.9 | 6.7 | 6.9 | 31.3 | 11.0 | 0.8 | 0.9 | 9.3 | 1.0 | 1.8 | 3.9 |

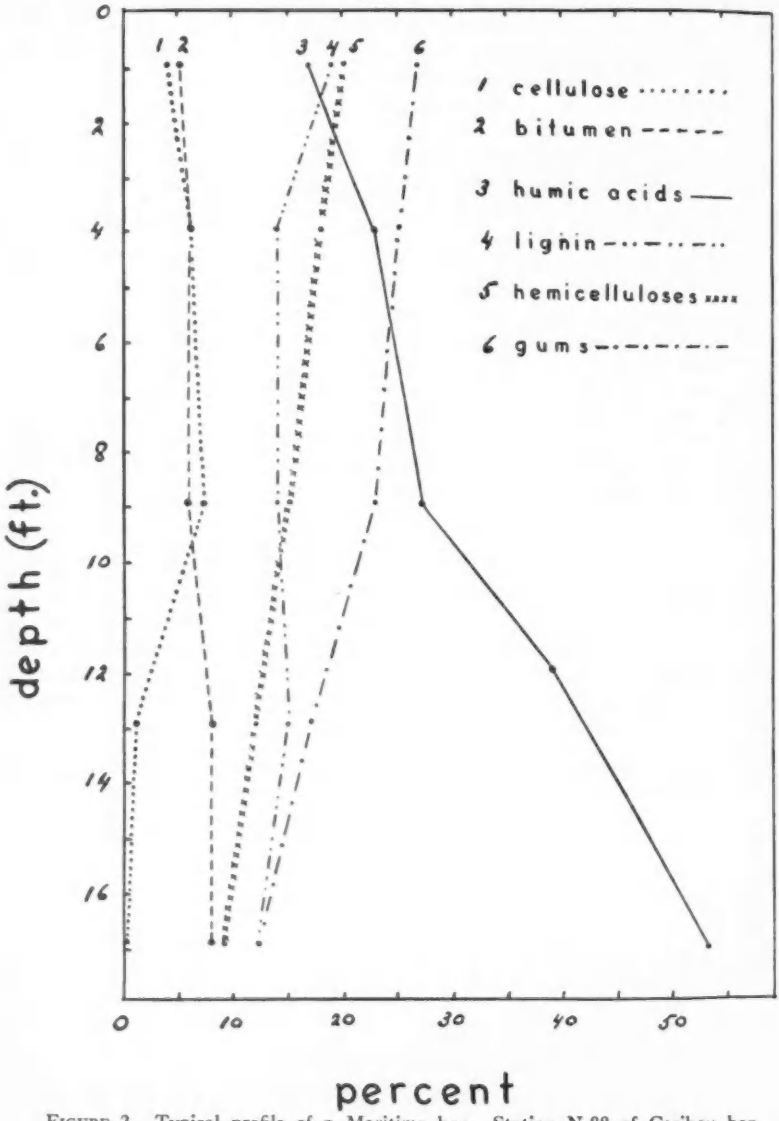



FIGURE 2. Typical profile of a Maritime bog. Station N-88 of Caribou bog, Nova Scotia.

The levels for total ash exhibited maxima either at the bottom or at the surface. Of the metallic elements determined, calcium predominated.

A typical profile (N-88) is shown in Figure 2 in which it is apparent that humic substances are formed by decomposition of the carbohydrates present, especially gums, hemicelluloses and possibly lignin.

TABLE 3.—CHEMICAL COMPOSITION OF PEAT FROM BOGS IN PRINCE EDWARD ISLAND

| Constituents | East Bideford | | Black Banks | | Portage | | Black Marsh | |
|---|---|---|---|---|---|---|---|---|
| | Range | Av. | Range | Av. | Range | Av. | Range | Av. |
| pH | 4.4–4.7 | 4.6 | 4.5–4.7 | 4.6 | 3.9–4.2 | 4.2 | 4.6–5.0 | 4.6 |
| Moisture | 84.6–95.8 | 92.6 | 90.0–97.0 | 93.9 | 89.3–96.0 | 93.2 | | |
| Organic[1] | | | | | | | | |
| Bitumen | 4.2–12.0 | 7.0 | 3.8– 7.8 | 6.2 | 4.0– 6.8 | 5.1 | 3.6–14.1 | 7.3[3] |
| Hemicelluloses | 5.2–19.9 | 14.7 | 13.9–22.2 | 18.7 | 6.8–23.5 | 13.9 | 1.5–22.8 | 13[3] |
| Other substances sol in HCl (2%) | 13.6–32.9 | 24.1 | 18.6–29.3 | 22.9 | 13.6–43.4 | 24.7 | 5.7–37.1 | 22[3] |
| Cellulose | 0.5–12.6 | 6.1 | 2.0–11.6 | 6.6 | 0.4–8.8 | 4.5 | 0.6– 7.5 | 2.8[3] |
| Other substances sol. in $H_2SO_4$ (18%) | 6.4– 9.2 | 7.6 | 6.2–11.4 | 8.5 | 3.6–9.7 | 6.2 | 4.1–19.1 | 10[3] |
| Humic acids | 8.7–52.0 | 27.2 | 17.5–34.6 | 27.7 | 5.0–60.8 | 28.3 | 1.8–45.6 | 34[3] |
| Lignin | 6.4–25.6 | 13.0 | 7.6–12.0 | 9.4 | 6.6–23.7 | 15.7 | 1.0–33.9 | 12[3] |
| Total N | 0.4–1.5 | 0.7 | 0.4– 1.0 | 0.6 | 0.6– 1.1 | 1.1 | 0.5– 2.2 | 1.6[3] |
| Total ash | 0.7– 1.6 | 1.0 | 0.8– 1.8 | 1.2 | 0.8– 2.9 | 1.5 | 2.3–44.2 | 16.7 |
| Inorganic[2] | | | | | | | | |
| Ca | 6.9–15.0 | 10.2 | 5.4–13.3 | 10.3 | 7.8–34.6 | 17.5 | 0.1–10.4 | 2.8 |
| Na | 1.5– 4.3 | 2.8 | 2.5–16.5 | 6.0 | 0.4– 1.0 | 1.0 | 0.1– 2.9 | 0.8 |
| K | 0.5– 0.9 | 0.6 | 0.4– 1.9 | 0.9 | 0.1– 1.8 | 0.4 | 0.4– 1.6 | 0.6 |
| P | 0.6– 2.0 | 1.3 | 0.9– 1.7 | 1.3 | 0.9– 1.8 | 1.2 | 0.1– 0.7 | 0.3 |

[1] As percentages of total solids
[2] Corrected for acid-insoluble ash
[3] As percentages of total ash

*New Brunswick*

The Lameque bog on the southern end of Shippigan Island is one of the largest deposits of high-grade peat moss in Canada. It consists of *Sphagnum fuscum* (Schimp) Klinngr., *S. capillaceum* (Weiss) Schrank, and *S. magnellanicum* Brid.*

The Shippigan bog is on the northeast point of the mainland in the same area. It contains essentially nothing but *Sphagnum fuscum* (Schimp.) Klinngr.*

The results of analyses are listed in Table 2. They are in general similar to those from the Caribou bog and indicate the same degree of humification. Samples were taken from these bogs at only five stations and the apparent constancy in composition at Shippigan is due to this limitation.

*Prince Edward Island*

Representative samples were taken from four bogs but not systematically as to depth. The depth of sampling varied from station to station. The analyses did not, therefore, give the true profile at any one station.

The two most important deposits of peat in P.E.I. are the East Bideford and Black Banks bogs. Samples of peat were also obtained from the Portage bog and the Black Marsh bog for exploratory reasons.

The analytical findings are reproduced in Table 3. Some samples contained sand, especially from the Black Marsh bog, and the final values were corrected for the acid-insoluble ash, when necessary, to make the results comparable.

* Identification through the courtesy of A. E. Porsild, Chief Botanist, and Curator of National Herbarium, National Museum, Ottawa, Ont.

## DISCUSSION

In discussing our findings it is appropriate to compare our results with the extensive analyses of Risi *et al.* (7), for the bogs of Quebec. All Maritime bogs examined were distinctly acid, mostly between pH 4.3 and 4.8, except the Portage bog and some parts of the Caribou bog which were between pH 3.9 and 4.2. In Quebec the acidity was between pH 4.9 and 5.6. The moisture content of 90 to 95 per cent is typical, except for the surface layer which is frequently lower in Quebec, but not in the Maritimes.

The ash content of Maritime peat was usually low at about 1 per cent even to depths of 16 feet, if not contaminated with earth or sand. This is much lower than in Quebec bogs. The major constituent of the ash of peat is aluminium silicate (7). Calcium was predominant of the alkali and alkaline earth metals determined. Phosphorus was present in small amount. Our results are very similar to those of Mitchell (5) for Scottish bogs at comparable depths and in proportions but not in magnitude to the Quebec bogs.

If the figures for the average composition of the seven Maritime bogs as listed in Tables 1, 2 and 3 be compared, some similarities and differences are apparent. In no bog does the content of bitumen average over 8 per cent, although below a depth of 8 feet in the Caribou and Lameque bogs it exceeds this figure. There is no information on the properties or composition of the bitumen fraction in these bogs. Increase in this fraction with depth was consistently observed in Maritime peats.

Total carbohydrate content in Maritime peats was about 60 per cent of the dry matter at the surface and about 25 per cent at 16 to 18 feet. The over-all average was 46 to 57 per cent. Comparison with the figures of Risi *et al.* (7) is difficult without recalculation on an ash-free basis because of the high values for ash in Quebec peats.

The average content of hemicelluloses was surprisingly constant at 14 per cent. It varied widely from about 20 per cent at the top to about 5 per cent at the bottom. Hemicelluloses were thus present in greater amount than in Quebec bogs. Other substances soluble in hot dilute hydrochloric acid comprised 20 to 25 per cent of the total solids and were most abundant at the surface. In the Portage bog a level of 43 per cent was observed. They decreased with depth as they did sometimes in Quebec bogs. The content of cellulose was usually highest in the upper layers but this varied considerably. Cellulose disappeared below 12 feet in some bogs. The over-all average was 6 per cent.

The concentration of lignin was very erratic as to depth. The over-all average was 12.7 per cent.

Organic nitrogen varied between 0.4 and 2.0 per cent, with an average of 0.9 per cent.

Humic substances comprised the largest analytical fraction and constituted the major products of humification. The over-all average was 29.4 per cent but the concentration below 10 feet was over 50 per cent in the Caribou bog. This fraction increased with the decrease in hemicelluloses and polyheteroglycans in Maritime bogs. This change was not nearly so consistent in Quebec bogs. Nevertheless, the accumulation of humic substances is indicated as the main process of humification. The changes in the

carbohydrate fractions observed with humification support the general observations of Theander (12). He noted losses in holocellulose and combined glucose, galactose, xylose, and uronic acids, but accumulations of mannose and rhamnose during humification. Fructose and arabinose disappeared. The relation of humic substances to these changes must await more knowledge of the chemical nature of these compounds.

It is obvious from the above analyses that the amounts of such substances as waxes, resins, cellulose, hemicelluloses, gums, lignin, and humic acids are enormous in our peat deposits. Whether they can be used for the commercial production of simple sugars, alcohols, acids, ketones, aldehydes, or other products, such as adhesives, activated carbons, resins or plastics, requires further investigations.

## ACKNOWLEDGEMENTS

We wish to express our gratitude for their co-operation in this project to F. A. Hogenson, of the Annapolis Valley Peat Moss Co. Ltd., to Em. Langevin of the Atlantic Peat Moss Co. Ltd., and to Graham Rogers, of the Department of Industry and Natural Resources, Prince Edward Island. We also wish to thank M. Archambault, of the Quebec Department of Mines, for the loan of a Davis sampler.

## REFERENCES

1. Association of Official Agricultural Chemists. Official methods of analysis. 8th ed. Washington, D.C. 1955.
2. Black, W. A. P., W. J. Cornhill, and F. N. Woodward. A preliminary investigation on the chemical composition of *Sphagnum* moss and peat. J. Appl. Chem. (London) 5:484-492. 1955.
3. Leverin, H. A. Peat moss deposits in Canada. Bur. Mines Publ. 817. Queen's Printer, Ottawa. 1946.
4. Leverin, H. A., and J. R. Cameron. Peat and peat mosses in Nova Scotia. N.S. Dept. Mines Annual Rept., pp. 187-264, 1947; pp. 143-174, 1948.
5. Mitchell, R. L. Trace elements in Scottish peats. Intern. Peat Symposium, Section B. 3, Bord na Móna, Dublin, Ireland. 1954.
6. Odén, S., and S. Lindberg. Einige Torfanalysen im Lichte neuzeitlicher Theorien der Kohlebildung. Brennstoff-Chem. 7:165-170. 1926.
7. Risi, J., C. E. Brunette, D. Spence, and H. Girard. A chemical study of the peats of Quebec. Dept. Mines, Quebec, P.R. 234, 1950; 281 and 282, 1953; 301, 1954; 306,1955.
8. Somogyi, M. Notes on sugar determinations. J. Biol. Chem. 195:19-23. 1952.
9. Souci, S. W. Beiträge zur chemischen Kennzeichnung und Analytischen Untersuchung des Torfes. Kolloid-Z. 82:87-99. 1938.
10. Swinnerton, A. A. Peat in Canada. Intern. Peat Symposium, Section A, Bord na Móna, Dublin, Ireland. 1954.
11. Theander, O. Studies on sphagnum peat. I. Preliminary studies on the carbohydrate constituents. Svensk Kem. Tidskr. 64:197-199. 1952.
12. Theander, O. Studies on sphagnum peat. III. A quantitative study on the carbohydrate constituents of sphagnum mosses and sphagnum peat. Acta Chem. Scand. 9:989-1000. 1954.
13. Vermynck, S. Contribution à l'étude et aux utilizations industrielles des tourbes françaises. Ann. mines 136:23-91. 1947.
14. Waksman, S. A., and K. R. Stevens. Contribution to the chemical composition of peat. II. Chemical composition of various peat profiles. Soil Sci. 26:239-251. 1928.

# SEASONAL pH FLUCTUATIONS IN A GREY WOODED SOIL[1]

W. E. BOWSER[2] AND J. N. LEAT[3]

*University of Alberta, Edmonton, Alberta*

[Received for publication January 24, 1958]

## ABSTRACT

Seasonal fluctuations in pH values were determined on soil samples from a modal Grey Wooded soil (Cooking Lake series). Samples were collected from the $A_o$, $A_2$, and $B_1$ horizons at regular intervals from May to November. During this period the pH of each horizon varied from neutral to strongly acid. These fluctuations appeared to be related to the soil moisture and possibly to the soil temperature regime.

## INTRODUCTION

Considerable variation in the pH values obtained among samples of the same soil series have been noted by the Alberta Soil Survey. Such variation might be due to inherent differences between the sampled profiles. However, since it is general practice for the Soil Survey to sample at any time throughout the summer field season, a wide variety of field climatic conditions would be represented and these might account for the pH variability.

Other workers have noted seasonal fluctuations in pH. In particular, Huberty and Haas (3) working at Riverside, California, with an irrigated soil, found a maximum seasonal fluctuation of about one pH unit. The greatest fluctuations were in the soil receiving the most frequent irrigations. Smith and Robertson (4), working in Scotland with fallow and cropped land, noted irregular fluctuations in pH as well as an over-all drop of slightly more than one pH unit during the midsummer season.

The study reported in this paper was undertaken to determine whether there was a significant seasonal variation in pH at a specific sample site.

## MATERIALS AND METHODS

Three plot sites were selected for this study. Site I was located 7 miles east of the city of Edmonton, in a gently rolling glacial moraine with aspen poplar as the main vegetative cover. The specific plot area was 8 feet square near the crown of a very gently sloping knoll. It had a 2 per cent slope to the northwest and was uniform as to soil type.

Site II was located approximately 30 miles east of Edmonton, on the western edge of Elk Island National Park. This site was similar in soil type, forest cover, and aspect to Site I. Site III was 1 mile east of Site I. It also was similar in soil type and aspect to Site I, but was cultivated. Site II was selected to check on the results obtained at Site I; and Site III was chosen for the purpose of comparing results obtained in a native soil with those from a similar cultivated soil. The soil on all plots was modal Grey Wooded: the Cooking Lake series (1).

[1] Contribution from Canada Soil Survey, University of Alberta, Edmonton, Alta. (Some of these data were presented by Mr. Leat to the Canadian Society of Soil Science meetings, June, 1955).
[2] Senior Pedologist.
[3] Pedologist (deceased).

The following is a description of the profile at Site I:

$A_0$ horizon—2″—0″ Upper portion relatively undecomposed leaves; lower portion partly decomposed organic debris.
$A_1$ horizon—0″—¼″ Loose, dark grey, loam
$A_2$ horizon—¼″—3″ Platy and somewhat porous, very pale brown fine sandy loam to light silt loam.
$B_1$ horizon—3″—6″ Friable blocky with pronounced horizontal cleavage lines. Pale brown to brown loam.
$B_2$ horizon 6″—16″ Firm medium sub-angular blocky, brown, clay loam. Some organic staining along cleavage faces.
$B_3$ horizon 16″—36″ Medium to large blocky becoming massive in the lower portion. Brown to dark brown clay loam.

The sampling was done at Site I during the growing seasons of 1954 and 1955; at Site II during the fall of 1956 and the spring and early summer of 1957, and at Site III during the growing season of 1955. Samples were taken with a 1¼-inch hand thrust coring auger and the $A_0$, the $A_2$, and the $B_1$ horizons were obtained from the removed cores. At Site III, however, the ploughed layer was taken instead of the $A_0$ and $A_2$ horizons. Four separate thrusts were made at random across each plot, and the samples were composited. This procedure, together with the smallness and uniformity of the plots, was planned to give the greatest practical uniformity of soil material throughout the sampling period.

Samples at Sites I and III were taken once a week from May to October, at 2.30 to 3.00 o'clock in the afternoon. The samples at Site II were taken at irregular intervals—some following heavy rains, and others after prolonged dry periods. The composite samples were placed in air-tight containers and taken immediately to the laboratory for pH and moisture determinations. The pH was determined with a glass electrode using a soil paste (2). Part of each sample collected during the first 3 months of 1954 was air-dried and the pH again determined. The soil temperature, at a depth of 2 inches in the mineral soil, was taken at the time of sampling.

The daily precipitation and temperatures as recorded at the Edmonton Airport were obtained from the Meteorological Service, Canada Department of Transport. In general, these meteorological data would be applicable to Sample Sites I and III.

## RESULTS

Most of the data obtained during 1954 and 1955 on Site I are reported graphically in Figures 1 and 2. These data indicate the following:

(a) There was considerable fluctuation of pH value in this soil during the growing season. Over the two seasons the pH of the $A_0$ varied from a maximum of 7.8 to a minimum of 5.8; a range of 2.0 pH units. The pH of the $A_2$ varied from a maximum of 7.0 to a minimum of 5.1; a range of 1.9 pH units. The pH of the $B_1$ varied from a maximum of 7.2 to a minimum of 5.3; a range of 1.9 pH units. A value of pH 7.7 for the $B_1$ horizon on October 22, 1955, was excluded from the above ranges because it was at considerable variance with the values of the other horizons as well as for the $B_1$ horizon at all other sampling dates.

(b) The $A_0$ had a consistently higher pH than either the $A_2$ or the $B_1$ horizon.

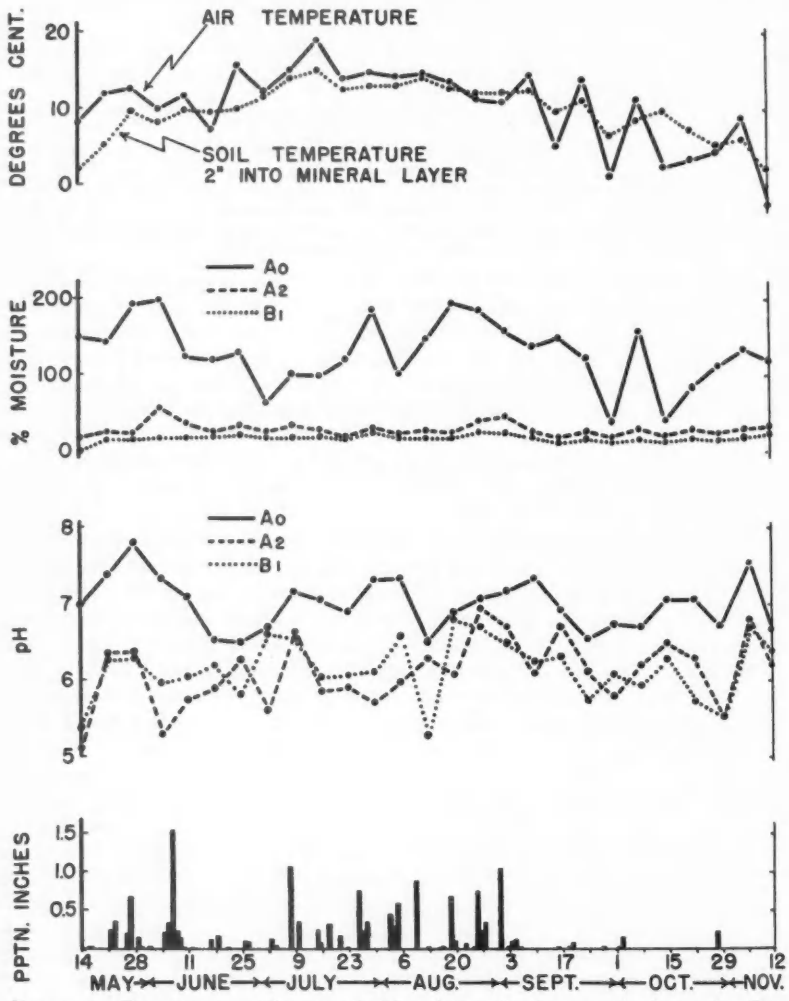



FIGURE 1. Temperature, moisture and pH variations in the upper horizons of a Grey Wooded soil in 1954.

(c) In both years there was a substantial increase in the pH of all three horizons immediately following the spring thaw.

(d) There is some indication of "waves" of acidity moving down the profile. This may be associated with the moisture regime.

The samples from Site II also varied considerably in pH value. The pH of the $A_0$ varied from 6.9 to 5.1, that of the $A_2$ from 6.6 to 5.4, and that of the $B_1$ from 6.4 to 4.9. The lowest values in all three horizons were obtained on samples taken following a week of very rainy weather.

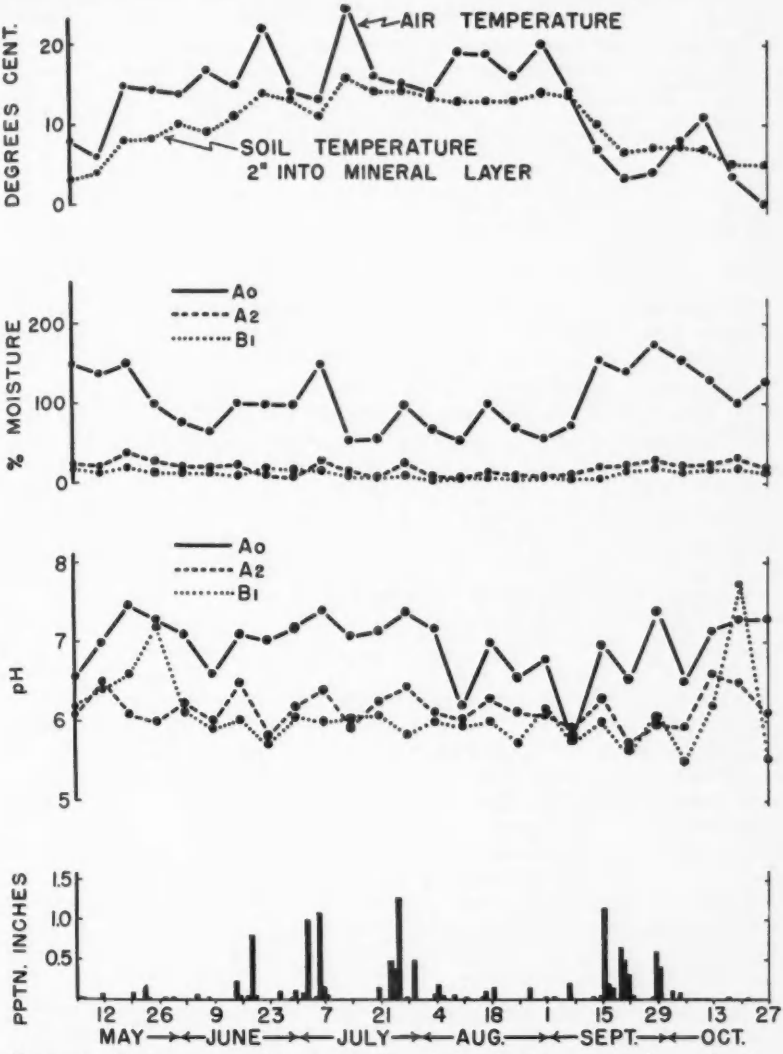



FIGURE 2. Temperature, moisture and pH variations in the upper horizons of a Grey Wooded soil in 1955.

As previously mentioned, the pH was also determined on some of the air-dried samples from Site I. In 44 out of 48 determinations, these had a lower pH than did the moist samples on which the determination was made immediately. The pH of the dried $A_0$ samples averaged 0.5 of a pH unit lower than those analysed immediately; those of the $A_2$ averaged 0.3 of a unit lower, and those of the $B_1$ averaged 0.2 of a unit lower. The pH was

TABLE I.—RANGE IN pH VALUES OBTAINED THROUGHOUT THE SAMPLING PERIODS

| Horizon | Site I (Native) | | Site II (Native) | | Site III (Cultivated) |
|---|---|---|---|---|---|
| | pH determined immediately (1954–55) | pH determined after air-drying (1954) | pH determined immediately (1956–57) | pH determined after air-drying (1956–57) | pH determined immediately (1955) |
| $A_0$ | 7.8 – 5.8 | 7.3 – 5.8 | 6.9 – 5.1 | 7.4 – 5.2 | ($A_p$) 7.7 – 6.8 |
| $A_2$ | 7.0 – 5.1 | 6.1 – 5.0 | 6.6 – 5.4 | 6.7 – 5.3 | |
| $B_1$ | 7.2 – 5.3 | 6.7 – 5.7 | 6.4 – 4.9 | 6.7 – 4.8 | 7.8 – 6.6 |

also determined on the dried samples from Site II. The pH on these $A_0$ samples averaged 0.2 of a pH unit higher than on the samples analysed immediately and the $A_2$ and $B_1$ samples averaged 0.1 of a pH unit higher.

As stated above, during 1955 samples were taken in a nearby cultivated field, where soil temperature was consistently higher than the temperature of the soil under native vegetation. The weekly recordings taken at the cultivated plot averaged 16.3° C. for the growing season, as compared to 10.5° C. at the native plot. The moisture content of the ploughed layer was almost identical with that of the $A_2$ of the native soil. The recorded pH range was narrower in the cultivated field. The pH of the ploughed layer fluctuated from 7.7 to 6.8, and that of the $B_1$ horizon from 7.8 to 6.6. A summary of these pH data is reported in Table I.

## DISCUSSION

This study was primarily outlined for the purpose of determining the seasonal pH fluctuations in a Grey Wooded soil at a specific sample site. It was not designed to determine the reasons for such fluctuations. It would appear, however, that they are related to changes in temperature and moisture and, therefore, possibly to microbiological activity. The data for soil moisture and pH in the $A_0$ horizon at Site I were analysed statistically. No significant correlations were found. The 1955 data, however, came closer to showing a significant correlation giving $r_{xy} = +0.330$: for significance at the 5 per cent level $r_{xy}$ should equal $+0.388$. It is suggested that, had the sampling been done relative to varying moisture contents rather than at a specific time each week, a significant correlation might have been obtained.

It should be noted that the soil studied was podzolic and had an $A_0$ horizon; therefore, the data are not necessarily applicable to other types of soil. This study does, however, suggest to the Soil Survey the following precautions:

(a) That in characterizing the horizons of a soil type, ranges of pH should be reported rather than a specific figure.
(b) That pH values at wide variance from the average should be discounted.
(c) That samples for characterization purposes should not be taken when extremes of soil moisture conditions exist.

## ACKNOWLEDGEMENTS

Acknowledgement is made to A. A. Kjearsgaard for preparing the graphs; to A. Leahey and C. F. Bentley for criticism of the original manuscript; and to S. Zalik for assistance with the statistical analyses.

## REFERENCES

1. Bowser, W. E., R. L. Erdman, F. A. Wyatt, and J. D. Newton. Soil survey of Peace Hills sheet. Rept. 14, Alberta Soil Survey, Edmonton, Alta. 1947.
2. Doughty, J. L. The advantages of a soil paste for routine pH determinations. Sci. Agr. 22: 135-138. 1941.
3. Huberty, M. R., and A. R. C. Haas. The pH of soil as affected by soil moisture and other factors. Soil Sci. 49: 453-478. 1940.
4. Smith, A. M., and I. M. Robertson. The influence of the plant upon seasonal changes in soil acidity. J. Agr. Sci. 21: 822-831. 1931.

# INFLUENCE OF SOIL TEXTURE, REACTION, AND TEMPERATURE ON THE UPTAKE OF NITROGEN FROM THREE NITROGEN FERTILIZERS[1]

C. S. BALDWIN AND J. W. KETCHESON[2]

*Ontario Agricultural College, Guelph, Ontario*

[Received for publication March 6, 1958]

## ABSTRACT

Rye grass was grown on four soils varying in texture and pH, in half-gallon glazed pots for a period of 8 months in the greenhouse. A 6-week cool period at 35° F. was employed following the first cutting. Nitrogen was top-dressed at the rate of 80 lb. nitrogen/ac., in the form of either urea, ammonium sulphate or calcium nitrate. These materials were added after germination of the ryegrass in one treatment, and beginning the cool period in a second treatment.

From 50 to 100 per cent of the added nitrogen was recovered in plant material and leachates. Calcium nitrate gave the highest recovery of nitrogen on all soils. No difference was found between ammonium sulphate and urea in the uptake and leaching of nitrogen. Urea was converted to ammonia, at temperatures as low as 35° F. The application of nitrogen before the cooling period extended the period of uptake by the crop.

It was concluded that the behaviour of nitrogen fertilizers in soil is dependent on both the texture and reaction of the soil, that the movement of urea in soil is small, and that the time of application influences the subsequent utilization of these materials by the crop.

## INTRODUCTION

Nitrogen uptake by plants may be influenced by soil texture and reaction, by temperature and moisture conditions, and by the form of nitrogen applied. The optimum time of application depends on the seasonal requirements of the crop, the period required to convert unavailable to available forms, and the possibility of loss following application. Fall applications of nitrogen may present technical as well as economic advantages, but losses through leaching may occur before utilization. Fertilizers carrying all or part of their nitrogen in the form of nitrate are considered to leach more readily than those consisting of ammonium nitrogen only. Urea nitrogen on the other hand may leach to varying depths before it is converted to the ammonium form. This paper reports the influence of soil texture, reaction, and a cooling period on the movement, transformation, and uptake of nitrogen from urea, ammonium sulphate, and calcium nitrate fertilizers.

Urea has been reported to nitrify more rapidly than ammonium sulphate in acid soils (7) due to the increase in pH associated with its hydrolysis. The time required for the nitrification of ammonium sulphate is thought to make it more slowly available to plants than nitrate nitrogen (8). Naftel (4) reports, however, that with optimum conditions appreciable amounts of nitrates are formed within a few days following an application of ammonium nitrogen. Ammonium nitrate applied as a top-dressing under dry conditions on the other hand remained on the surface completely unnitrified after 25 days (3).

[1] Contribution from the Department of Soils, Ontario Agricultural College, Guelph, Ont.
[2] Graduate student (now at Western Ontario Agricultural School, Ridgetown, Ont.), and Assistant Professor, respectively.

Nitrates have been found to penetrate to and accumulate at the 24-inch depth when a fine sandy loam was leached with 12 inches of water (5). Jenny *et al.* (2) have shown that ammonium nitrogen applied in irrigation water on soil columns penetrated to a depth of 6 inches in sands, to 4 inches in sandy loams, and to 2 inches in clay soils. Allison (1) found that nitrogen in the form of urea would leach from a sandy soil within 4 days following application.

While soil reaction is reported to affect nitrification of certain nitrogen fertilizers and finer textured soils appear to reduce the leaching of nitrates, detailed evidence pertaining to the behaviour of these fertilizers is lacking in the literature. Most temperature effects reported are related to nitrification rates, but do not indicate the effect of cool periods on uptake by plants.

## MATERIALS AND METHODS

The soils used in this study were surface samples of Schomberg silt loam (pH 7.8 and O.M. 3.5 per cent), Bondhead sandy loam (pH 7.2 and O.M. 4.5 per cent), Oneida clay loam (pH 6.6 and O.M. 2.7 per cent), and Fox sandy loam (pH 6.2 and O.M. 3.7 per cent). The first two were selected to represent alkaline soils and the second two acid soils. The Schomberg and Oneida were chosen to represent a fine textured group, and the Bondhead and Fox a coarse textured group. All were of grey-brown podsolic development.

Half-gallon glazed pots were filled with moist soil equivalent to 5 lb. of oven-dry soil, and placed in the greenhouse. Immediately prior to potting and planting, and based on their requirements, the fine textured soils were fertilized throughout the pot with phosphorus and potassium at the rate of 80 and 120 lb. per acre, and the coarse textured soils at the rate of 60 and 180 lb. per acre, respectively. Ten Italian ryegrass seedlings were grown in each pot.

The soils were watered to approximately field capacity every 7 days and additions were made during this period as conditions necessitated. Temperature in the greenhouse ranged from approximately 60° F. to 105° F.

The nitrogen fertilizers used in this study were urea (45 per cent N), ammonium sulphate (20 per cent N), and calcium nitrate (17 per cent N) and were selected to represent three distinct types which might differ most in behaviour. They were top-dressed at each of two application dates at the rate of 80 lb. N per acre. An after-germination application was applied 2 weeks after emergence of the ryegrass to one group of nine pots in each replicate, and a before-cooling application was applied to a second group of nine pots immediately after the first cutting and prior to placing all pots in a cool chamber at 35° F. for a 6-week period. Control pots with no added nitrogen were provided. A randomized block design with three replications was used in arranging the treatments on the greenhouse bench.

Four cuttings were removed with approximately a 2-month interval between each. Each pot was leached following the first cutting, following the cool period, and following the last cutting, with 750 ml. of distilled water (2¼ inch) on each occasion. The roots were removed from the soil

TABLE 1.—DRY MATTER YIELDS IN POUNDS PER ACRE AND NITROGEN PERCENTAGES OF ABOVE-GROUND PLANT MATERIAL FOR FOUR SOILS AND TWO NITROGEN APPLICATION TIMES. (THREE SOURCES OF NITROGEN AVERAGED)

| Soil and Fertilizer Application Time | | Cutting | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4* | Total |
| *Schomberg* | – after germination | 1552 (4.67)** | 1457 (2.61) | 1540 (1.11) | 2507 (0.85) | 7056 |
| | – before cooling (between cuttings 1 and 2) | 1641 (3.75) | 1732 (3.11) | 1750 (1.06) | 2520 (0.86) | 7643 |
| | – no nitrogen | 1641 (3.75) | 885 (1.84) | 1106 (1.09) | 2234 (0.85) | 5866 |
| *Oneida* | – after germination | 2063 (3.77) | 666 (1.80) | 839 (1.09) | 1485 (0.96) | 5053 |
| | – before cooling | 1201 (2.15) | 1379 (2.48) | 1364 (1.04) | 1761 (0.81) | 5705 |
| | – no nitrogen | 1201 (2.15) | 356 (1.97) | 803 (1.24) | 1583 (1.01) | 3943 |
| *Bondhead* | – after germination | 2222 (3.85) | 896 (2.32) | 1250 (1.26) | 2445 (1.07) | 6813 |
| | – before cooling | 1540 (2.52) | 1426 (3.23) | 1522 (1.19) | 2546 (1.03) | 7034 |
| | – no nitrogen | 1540 (2.52) | 730 (2.07) | 1151 (1.26) | 2151 (1.12) | 5578 |
| *Fox* | – after germination | 1894 (3.93) | 688 (1.56) | 659 (0.99) | 1273 (0.87) | 4514 |
| | – before cooling | 1232 (2.62) | 1311 (2.53) | 1086 (1.00) | 1437 (0.88) | 5066 |
| | – no nitrogen | 1232 (2.62) | 292 (1.76) | 556 (1.17) | 1177 (0.97) | 3257 |

* Cutting 4 includes stubble from all cuttings.
** Nitrogen percentage shown in brackets.

at the conclusion of the growing period, all plant material dried at 85° C., weighed, and analysed for total nitrogen. The leachates were analysed for urea, ammonium, and nitrate nitrogen. Nitrate and ammonium nitrogen in the soil leachates and the total nitrogen in the plant material were determined by methods outlined by Prince (6). Urea was hydrolysed to ammonia with the enzyme urease from jack bean meal.

## RESULTS AND DISCUSSION

Dry matter yields and nitrogen percentages of above-ground plant material for the four soils and the two application dates are given in Table I. On all soils the before-cooling fertilizer applications yielded more dry matter than those applied after germination. Fertilizer applied before cooling on the Fox soil gave the highest increase of dry matter over check yields (1809 lb. per acre), whereas the lowest increase resulted from fertilizer applied after germination on the Oneida soil (1110 lb. per acre).

With the after-germination fertilizer treatment, and on all soils except the Schomberg, the greatest response was obtained in the first cutting following the application. Fertilizer applied before the cool period did not give this type of response as the four cuttings were more uniform. This suggests that the fertilizer was more slowly available from the before-cooling application than from the after-germination application. For each soil, regardless of the fertilizer used, the per cent nitrogen of the plant material was similar with the highest values associated with cuttings immediately following the nitrogen application. In all soils and for each fertilizer the nitrogen percentages had levelled off by the fourth cutting. The high yield and nitrogen percentage associated with the after-germin-

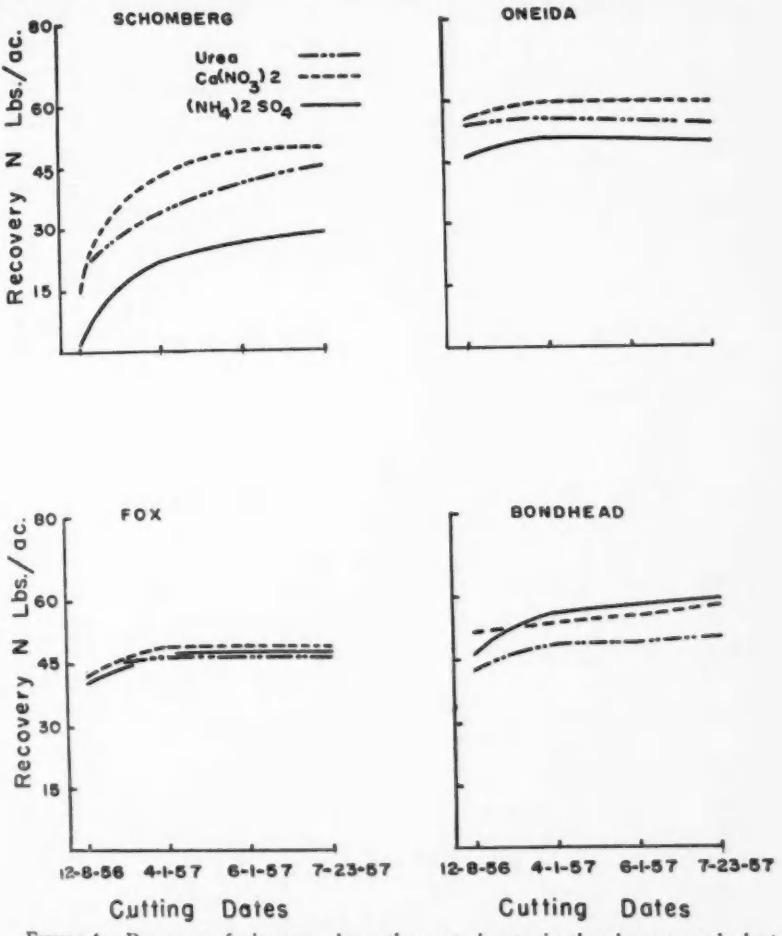



FIGURE 1. Recovery of nitrogen, above the control pots, in the above-ground plant material. Nitrogen fertilizer applied after germination.

ation treatment suggests the possibility of "luxury" consumption and could account for the lower total yield through unnecessary depletion of the nitrogen supply.

Nitrogen uptake for the various treatments was calculated from yield and nitrogen percentage. In the statistical analysis of the nitrogen uptake data the interaction of texture x reaction x fertilizers x application dates was significant. This precluded direct comparisons of main effects without qualification with respect to the other interrelated factors.

From Figures 1 and 2 it is evident that the recovery of nitrogen above the control pots in the above-ground plant material varies both with soil and time of application. The only treatments statistically different at

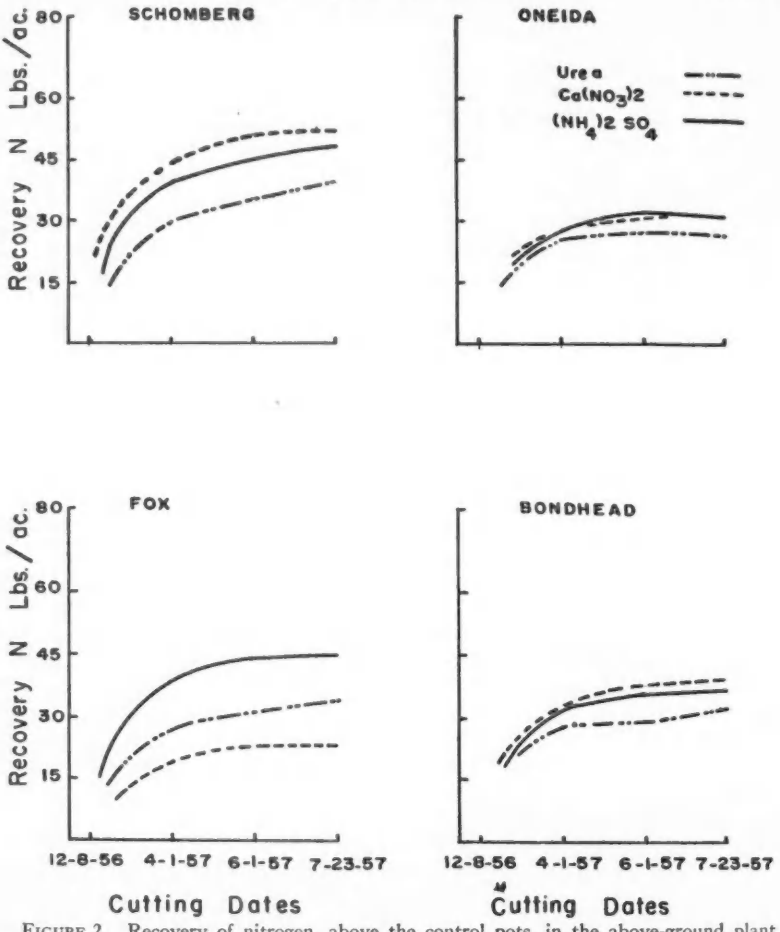



FIGURE 2. Recovery of nitrogen, above the control pots, in the above-ground plant material. Nitrogen fertilizer applied before cooling.

the 5 per cent level are the calcium nitrate and ammonium sulphate applied after germination on the Schomberg (Figure 1) and before cooling on the Fox (Figure 2). The calcium nitrate is higher in the former case and lower in the latter. The reason for this reversal may be due in part to nearly one-half of the fertilizer nitrogen leaching from the Fox soil following the cool period. It is also evident from these figures that the Schomberg soil gives a gradual uptake while the other three give a higher uptake in the cuttings immediately following the nitrogen application. The untreated Schomberg soil yielded the highest nitrogen of the four soils and this could account for the more gradual uptake exhibited by this soil.

The recovery of nitrogen above the control pots in the leachates is given in Figures 3 and 4 and was highest on the Schomberg soil. The

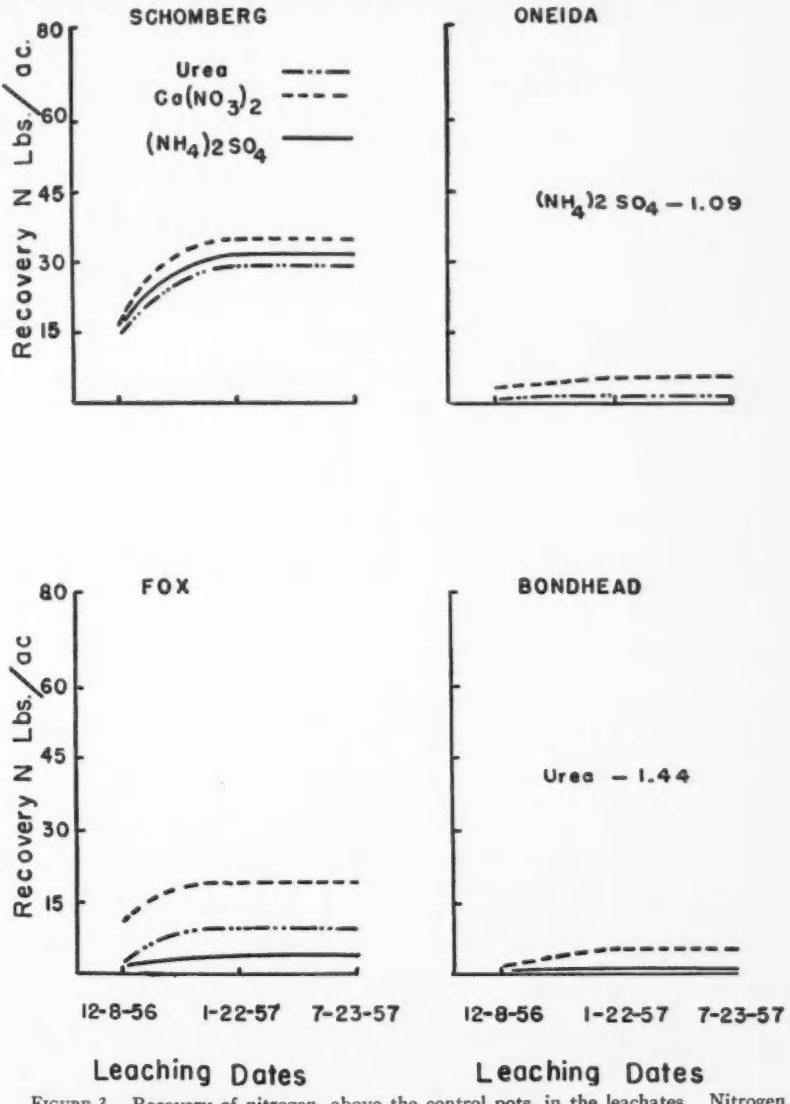



FIGURE 3. Recovery of nitrogen, above the control pots, in the leachates. Nitrogen fertilizer applied after germination.

possibility of reduced adsorption of ammonia and nitrate on this alkaline soil may be a contributing factor. Significantly more nitrate nitrogen leached from calcium nitrate treated pots than from either of the other fertilizers, but there was no statistically significant difference between the amounts leached from ammonium sulphate and urea.

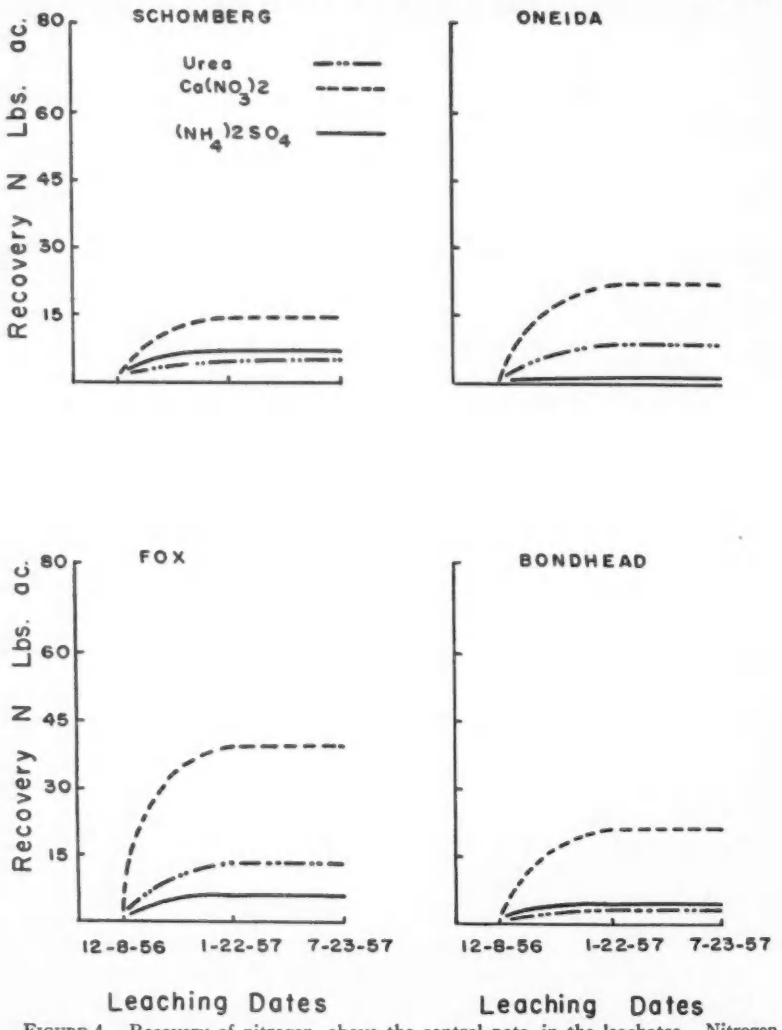



FIGURE 4. Recovery of nitrogen, above the control pots, in the leachates. Nitrogen fertilizer applied before cooling.

On the Fox soil with the before-cooling treatment almost one-half of the nitrogen from calcium nitrate was accounted for in the leaching immediately following the cool period. This observation was associated earlier with the low yield of dry matter on this treatment. On the Schomberg soil over twice the amount of nitrogen was leached from all three fertilizers applied after germination as when applied before the cool period. This may mean that adsorption and uptake can be appreciable during dormant periods.

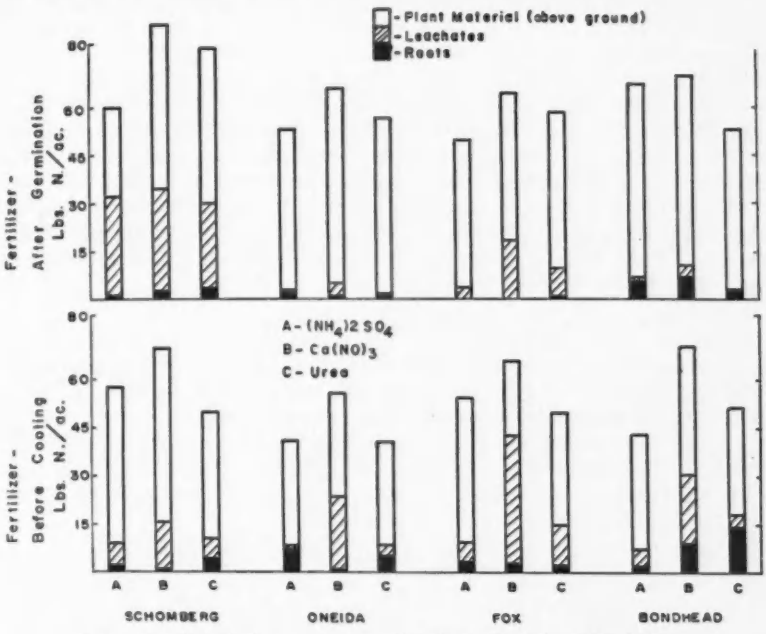

- Plant Material (above ground)
- Leachates
- Roots
Fertilizer - After Germination Lbs. N./ac.
Fertilizer - Before Cooling Lbs. N./ac.
A - $(NH_4)2SO_4$
B - $Ca(NO)_3$
C - Urea
A B C A B C A B C A B C
SCHOMBERG ONEIDA FOX BONDHEAD

FIGURE 5. Total nitrogen recovered in plant material and leachates.

Urea was not found in any of the three leachings. This suggests that conversion had taken place, even at the 35° F. temperature. With only a small amount of nitrate and no urea appearing in the leaching following the cool period of the before-cooling treatment, it is evident that nitrogen from this fertilizer was effectively held, either by plant roots, micro-organisms, or soil colloids, even under adverse conditions. The amount of nitrogen recovered above the control pots in the roots was approximately only one-thirteenth that of the above-ground plant material. On the Bondhead soil, however, the root material accounted for better than one-sixth the amount.

The total nitrogen recovered in plant material and leachates is shown in Figure 5. The recovery of the initial 80 lb. per acre application, assuming the soil supply from the treated pots was the same as the untreated pots, ranged from approximately 50 to 100 per cent. The calcium nitrate in all cases yielded the highest recovery of nitrogen within soils. Urea and ammonium sulphate were variable in their behaviour.

It would appear, therefore, that the nitrate form, even though it is more subject to leaching, is the most efficiently used by plants. This is in keeping with the work reported in the literature regarding the preferential absorption of nitrate nitrogen by plants.

Urea and ammonium sulphate act similarly for the method of application used in this study and this may be explained through the rapidity with which the former is transformed into the ammonium form by the

urease activity in the soil. If this activity is restricted for any reason, the two materials might be expected to behave differently. Banded urea for instance presumably draws its enzyme supply from a restricted volume of soil and this may result in delayed conversion. The extent to which urea can move from the point of application will depend on moisture movement and conversion. Banding, therefore, may retain urea in this form until it is dissipated sufficiently to contact enzyme for its conversion. The possibility of urea being carried an appreciable distance from the surface into the rooting zone would appear small from the results of this study. Other factors restricting urease activity or the conversion of urea have yet to be investigated.

## CONCLUSIONS

It may be concluded that the kind of fertilizer, temperature conditions following application, and the texture and reaction of the soil should all be considered in planning nitrogen fertilizer treatments.

Urea and ammonium forms of fertilizer may be expected to exhibit lower leaching losses than nitrate forms. Losses should be at a minimum when soil temperatures following application are in the region of 35° F. and a living crop is established in the soil.

Urea may be carried into the rooting zone by leaching, but this movement is limited even at 35° F. by the rapidity with which it is converted to ammonium forms. It is not likely to leach beyond the reach of roots.

Nitrate nitrogen which remains in the rooting zone can be expected to be used more efficiently than other forms.

A high level of applied nitrogen early in the growth of a crop may result in abnormally high uptake without corresponding yield increases in the initial harvests, and with low yields in the final harvests. Timeliness in application dates can overcome this effect.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge assistance from the Toronto Anglers' and Hunters' Association.

## REFERENCES

1. Allison, R. V. Leaching studies from Florida soils with various sources of nitrogen. Commercial Fertilizers 59:12. 1939.
2. Jenny, H., A. D. Ayers, and J. S. Hosking. Comparative behavior of ammonia and ammonia salts in soils. Hilgardia 16:429-47. 1945.
3. Krantz, B. A., *et al.* Movement of nitrogen in soils. Soil Sci. Soc. Amer. Proc. 8: 189-195. 1943.
4. Naftel, J. A. The nitrification of ammonium sulphate as influenced by soil reaction and degree of base saturation. J. Amer. Soc. Agron. 23:175-185. 1931.
5. Nelson, C. E. Methods of applying ammonium nitrate fertilizer on field corn and a study of the movement of $NH^{4+}$ - and $NO^{3-}$ - nitrogen in soils under irrigation. Agron. J. 45:154-157. 1953.
6. Prince, A. L. Determination of total nitrogen, ammonia, nitrates, and nitrites in soils. Soil Sci. 59:47-53. 1945.
7. Soubries, L., *et al.* Investigations on the evolution of urea in soils and its use as a nitrogen fertilizer. (*Abstract*). Soils and Fertilizers 19:285. 1955.
8. Tiedjens, V. A., and W. R. Robbins. The use of ammonia and nitrate nitrogen by certain crop plants. New Jersey Agr. Expt. Sta. Bull. 526. 1931.

# THE EFFECT OF SOIL AGGREGATE SIZE ON AVAILABILITY OF OXYGEN AND ON GROWTH OF TOMATOES

J. J. DOYLE AND A. A. MACLEAN

*Canada Department of Agriculture, Fredericton, New Brunswick*

[Received for publication February 21, 1958]

## ABSTRACT

Diffusion of oxygen was measured by the platinum micro-electrode method on seven sizes of artificially prepared soil aggregates. Diffusion of oxygen was directly proportional to aggregate size.

Growth of tomato plants increased with aggregate size and with diffusion rate of oxygen.

For a temperature of 68° F., and with the surface of the soil at a moisture tension of 20 cm., critical diffusion rates of oxygen are suggested for the 2-, 4- and 6-inch depths of $12\times10^{-7}$, $8\times10^{-7}$ and $6\times10^{-7}$ grams/cm²/min. respectively.

A thorough study of the performance of the platinum micro-electrode method under field conditions is recommended, with a view to adapting it for the direct assessment in the field of soil physical condition and for the establishment of critical levels of oxygen for crops.

## INTRODUCTION

Procedures used in the evaluation of soil structure are, in almost all cases, attempts to measure such properties as size of water stable aggregates, porosity, bulk density, permeability etc. These procedures have yielded very little quantitative data relating soil physical condition and plant growth. Some workers (8, 9) are of the opinion that the most promising approach to the evaluation of soil physical condition lies, not in the direct measurement of soil structure, but in the description of dependent properties such as air, water and temperature conditions. Since aeration is probably the most important condition affected by structure, availability of oxygen should provide a useful criterion of soil physical condition.

In order to obtain data relating soil aggregate size, availability of oxygen and plant growth, an experiment was conducted in the greenhouse using the platinum micro-electrode technique of Lemon and Erickson (6) to measure oxygen diffusion.

## MATERIALS AND METHODS

A silty clay loam soil was air-dried, passed through a half-inch sieve, mixed thoroughly with a synthetic soil conditioner and saturated with water. The soil was then dried, crushed and separated into the following size groups: 5-10, 2-5, 1-2, 0.5-1, 0.25-0.5, 0.1-0.25 and $<0.1$ mm. Analysis by the Yoder Method (6) showed that the aggregates were completely water-stable. Mechanical analysis (2) showed no textural differences between aggregate sizes. The soil was placed in 1-gallon glazed pots, which were set in shallow water pans with the surface of the soil at a moisture tension of 20 cm. The temperature of the soil was maintained at 68° F $\pm$ 5°. Five replicates of each treatment were used in a randomized block design.

When the soil was at equilibrium with the water table, oxygen diffusion was measured by the platinum micro-electrode method (6) at depths of 2, 4 and 6 inches. No further measurements were made because of the possibility that repeated punching of the soil by the electrodes might upset the diffusion readings. The soil temperature while diffusion was being measured was 68° F.

The soils were then planted to Early Chatham tomatoes which were harvested when small fruit began to develop.

## RESULTS AND DISCUSSION

The relationship between aggregate size and diffusion of oxygen is shown in Figure 1. The aggregation data are expressed by the mean weight-diameter method of Van Bavel (11). This method was used so that each size group could be expressed as a single numerical value. The linear relationship between diffusion and aggregate size was significant for the three depths at the 1 per cent level of probability. Diffusion of oxygen was, therefore, directly proportional to aggregate size. The same degree of correlation however, might not be obtained under the conditions of higher moisture tension ordinarily encountered in the field. With higher moisture tensions the electrode might not be completely moist, with the result that its effective area would be reduced and might be quite variable. It might be necessary, therefore, under field conditions to have the moisture content of the soil close to field capacity, to ensure correct determinations.

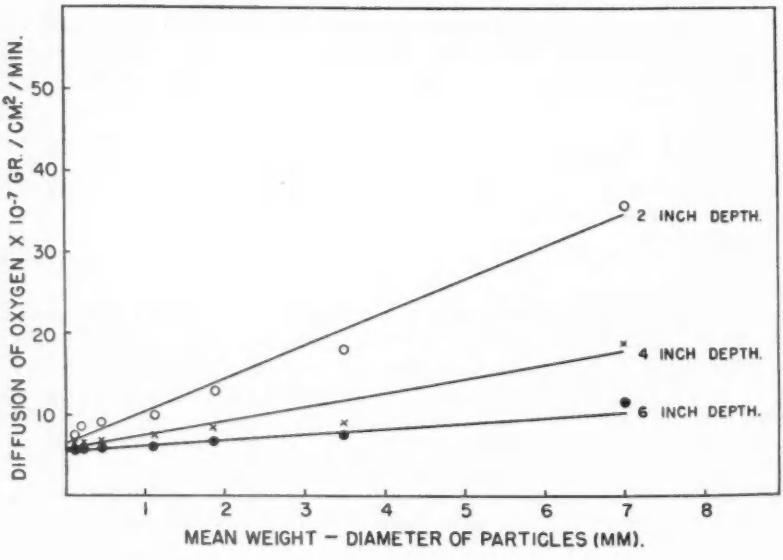



FIGURE 1. Effect of soil aggregation on diffusion of oxygen.

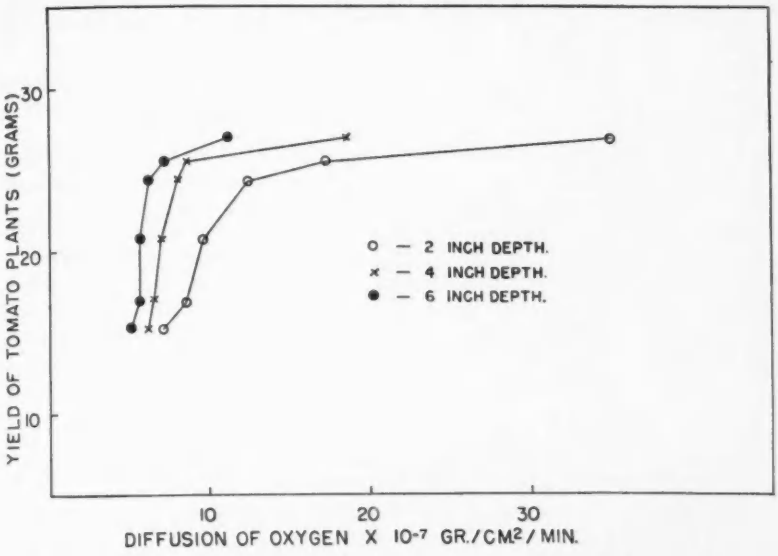



FIGURE 2. Relationship between availability of oxygen and growth of tomato plants.

Other factors which might influence the diffusion reading are temperature, pH, salt concentration and the valence of the ions in solution. These factors affect the velocity and the direction of water movement due to electro-osmosis (4, 5, 12). Obviously, since it is the oxygen in solution which is measured, movement of the soil solution in relation to the electrode might cause serious error. The high degree of correlation between aggregate size and diffusion obtained in this experiment and by other workers (1, 6) indicate, however, that the error due to electro-osmosis may be serious only under extreme conditions.

The decrease in diffusion with increasing depth is to be expected, since it has been well established that, where no water is applied to the surface, the moisture content of a soil increases as the water table is approached (3, 7) and that diffusion is a linear function of water-free porosity (10).

The response of tomato plants to oxygen is shown in Figure 2. The curves show a marked increase of growth with oxygen supply up to about $12 \times 10^{-7}$, $8 \times 10^{-7}$ and $6 \times 10^{-7}$ grams/cm$^2$/min at the 2-, 4- and 6-inch depths respectively. Since the response above these levels is relatively small, they are suggested as critical levels for tomatoes. These results are in fairly close agreement with the critical levels suggested by Lemon and Erickson (6) for tomatoes at the 8-inch depth and by Bertrand and Kohnke (1) for corn in the 8- to 16-inch layer. There are several factors, however, which might influence the oxygen requirements of a plant. Any factor such as temperature, light, moisture supply or soil fertility, which has an effect on the rate of growth or respiration of a plant, must have an effect on its oxygen requirement. Critical levels should, therefore, be studied further under varying conditions of soil productivity.

Another factor which will be encountered under field conditions is the presence of plant roots. Since respiration is almost certain to have an effect on diffusion for best results from use of the method it may be necessary to avoid the root zone entirely or to make the measurements when no plants are growing in the soil.

It is concluded that, under the conditions of this experiment, diffusion of oxygen was directly proportional to aggregate size and that the platinum micro-electrode made satisfactory measurements of the availability of oxygen to plants. It is suggested that *in situ* measurements of oxygen by this method be used to establish critical levels of oxygen for crops and for the assessment of soil physical condition. It is emphasized, however, that, before the method can be used with any degree of confidence under field conditions, a thorough study must be made of factors which might influence 1), the diffusion readings, and 2), the oxygen requirement of the crop.

## REFERENCES

1. Bertrand, A. R., and H. Kohnke. Subsoil conditions and their effects on oxygen supply and the growth of corn roots. Soil Sci. Soc. Amer. Proc. 21:135-140. 1957.
2. Bouyoucos J. C. A recalibration of the hydrometer method for making mechanical analysis of soils. Agron. J. 43:434-438. 1951.
3. Buckingham, E. Studies on the movement of soil moisture. U.S. Dept. Agr. Bur. Soils Bull. 38 1907.
4. Getman, F. H., and F. Daniels. Outlines of physical chemistry. John Wiley & Sons Inc., New York, N.Y. 1943.
5. Hartman, R. J. Colloid chemistry. Houghton Mifflin Co., Riverside Press, Cambridge, Mass. 1947.
6. Lemon, E. R., and A. E. Erickson. The measurement of oxygen diffusion in the soil with a platinum micro-electrode. Soil Sci. Soc. Amer. Proc. 16:160-163. 1952.
7. Richards, L. A. Methods of measuring soil moisture tension. Soil Sci. 68:95-112. 1949.
8. Russell, M. B. Methods of measuring soil structure and aeration. Soil Sci. 68:25-35. 1949.
9. Shaw, B. T. Soil physical conditions and plant growth. Academic Press Inc., New York, N.Y. 1952.
10. Taylor, S. A. Oxygen diffusion in porous media as a measure of soil aeration. Soil Sci. Soc. Amer. Proc. 14:55-61, 1949.
11. Van Bavel, C. H. M. Mean weight-diameter of soil aggregates as a statistical index of aggregation. Soil Sci. Soc. Amer. Proc. 14:20-23. 1949.
12. Weiser, H. B. Colloid chemistry. John Wiley & Sons Inc., New York, N.Y. 1948.
13. Yoder, R. E. A direct method of aggregate analysis and a study of the physical nature of erosion losses. J. Amer. Soc. Agron. 28:337-351. 1936.

# THE FORMS OF NITROGEN IN THE ORGANIC MATTER OF DIFFERENT HORIZONS OF SOIL PROFILES[1]

F. J. SOWDEN

*Canada Department of Agriculture, Ottawa, Ontario*

[Received for publication March 18, 1958]

## ABSTRACT

A study was made of the amount of amide-N (as glutamine and asparagine) in soil materials by methylating the organic material with methanolic-HCl, reducing the resulting product with $LiBH_4$ and determining the loss of glutamic and aspartic acids. The data obtained lend support to the hypothesis that a percentage of the ammonia-N formed on acid hydrolysis, equal or nearly equal to the sum of the glutamic acid-N + the aspartic acid-N, is derived from glutamine and asparagine. An attempt to use other methods to determine the amount of amide-N in soil materials indicated that these methods would not, in general, be reliable, although they might give acceptable results when the degree of decomposition of the organic materials was not too great (e.g., in the $A_{00}$ or $A_0$ horizons).

In a previous paper (15), it has been shown that from 20 to 45 per cent of the total-N in soils can be accounted for as amino acids and hence may be in the form of proteins or peptides. Most of the remainder of the nitrogen has still to be accounted for. A large amount of ammonia-N is formed on acid hydrolysis and it has been postulated that some of this may be present in soils as the amides of glutamic and aspartic acid. It would be of interest to find some experimental evidence for this hypothesis. A method for the determination of asparagine and glutamine in proteins has been developed by Chibnall and Rees (3). The method was adequately described by the above authors and by Fromageot and Jutisz (6). Briefly, the free carboxyl groups of the protein are esterified (usually by 0.1 N HCl in dry methanol) and the resulting esters reduced to the corresponding alcohols by the use of $LiBH_4$. Amides are not affected by this treatment; hence, if the amides of glutamic and aspartic acids occur in the materials being analysed they will be found in the acid hydrolyzates as glutamic or aspartic acids.

To illustrate the application of the method, part of the phenylalanyl chain of performic acid-oxidized insulin is shown in Figure 1. If one mole of this peptide is hydrolyzed, 1 mole of phenylalanine, 2 of valine, 1 of aspartic acid, 2 of glutamic acid, 2 of histidine, 3 of leucine, 1 of cysteic acid, 1 of glycine, 1 of serine, 1 of alanine and 2 of ammonia are formed. If the peptide is treated with methanolic-HCl, the free carboxyl groups of the $\alpha$-glutamyl residue and of the C-terminal leucine are esterified; on reduction with $LiBH_4$ the corresponding alcohols are formed. Hydrolysis of the reduced peptide would yield the same substances as listed above, except that only 1 mole of glutamic acid and 2 moles of leucine would be formed; the other glutamic acid and leucine residues would appear as $\delta$-hydroxy $\alpha$-aminovaleric acid and leucinol. This would show that all of the aspartic acid and half of the glutamic acid were present in the peptide

[1]Contribution No. 391, Chemistry Division, Science Service, Canada Department of Agriculture, Ottawa, Ont.

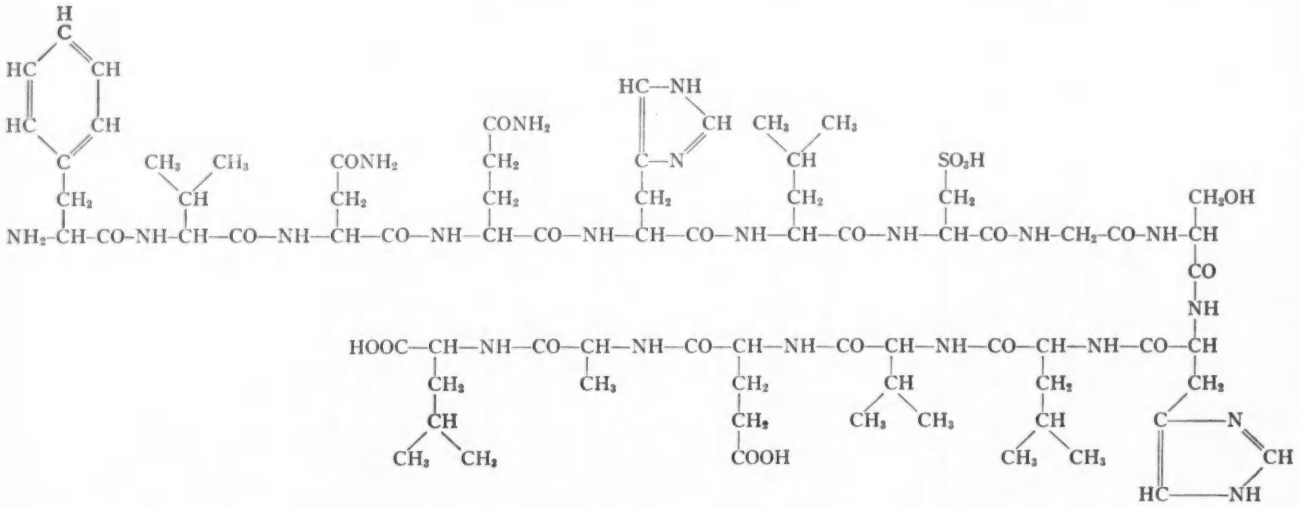


FIGURE 1—Part of the phenylalanyl chain of performic acid-oxidized insulin.

chain as amides. It should be noted that these reactions are not strictly quantitative; there is some loss of amide-N and some splitting of the peptide chain during treatment (4). However, these errors should not be of sufficient magnitude to affect the interpretation of the results of the application of this method to soil materials. If soil organic matter is methylated, reduced with $LiBH_4$ and hydrolyzed with acid, any decrease in the yields of glutamic and aspartic acids should give an indication of the amounts of glutamic and aspartic acid present in the original material. The yield of glutamic and aspartic acid would show the amount of amide. It should be noted that any amino acid occurring at the end of a peptide chain with its carboxyl group free would also be reduced and hence would not appear in the acid hydrolyzate as the free acid.

## MATERIALS AND METHODS

### *Materials*

The samples from a Cape Breton soil profile used in this investigation have been described previously (15). These samples were chosen because adequate data on their amino acid distribution were available, and the percentage of their total-N accounted for as amino acid-N varied from 25 to 42.

### *Ammonia Nitrogen*

This was determined by evaporating suitable aliquots of the hydrolyzates to dryness, adding water, making alkaline with MgO and distilling the ammonia into boric acid.

### *Methylation*

A modification of the method of Mommaerts and Neurath (12) was used. Suitable sized samples (2 to 10 gm.) were stirred with a mercury-sealed or a magnetic stirrer for 24 hours at room temperature in 200 ml. of dry methanol made 0.1 N with dry HCl. After 24 hours the suspension was poured into 500 ml. of ether, filtered and washed with ether. The recovered material was dried and weighed.

### *Reduction with $LiBH_4$*

1 to 7 gm. samples of the methylated materials were dried overnight, suspended in 20 to 30 ml. of tetrahydrofuran (previously distilled from NaOH and $LiAlH_4$ under dry $N_2$), 100 to 150 mgm. of $LiBH_4$ added under dry $N_2$ and the suspension stirred at room temperature overnight with a mercury-sealed stirrer. The $LiBH_4$ was decomposed with N HCl, the material filtered, washed with ether, and freed from ether. These methods were adapted from several papers (1, 2, 3, 5, 6, 7).

### *Hydrolysis*

The reduced material was hydrolyzed with 6 N HCl using about the same ratio of HCl to sample as was used previously (15).

### *Amides*

The amounts of amide-N were determined by the methods of Levy *et al.* (9) and Newton and Abraham (13).

TABLE 1.—DISTRIBUTION OF N IN HYDROLYZATE OF CAPE BRETON SOIL
(Per cent of total N)

| | N accounted for as amino acid-N | $NH_3$-N | Asp. and Glu.-N | $NH_3$-N not accounted for | Dissolved by acid hydrolysis |
|---|---|---|---|---|---|
| $A_{00}$ 6″—3″ | 41.8 | 13.2 | 9.2 | 4.0 | 87 |
| $A_0$ 3″—1″ | 40.4 | 15.7 | 9.5 | 6.2 | 86 |
| $A_0$ 1″—0″ | 34.4 | 15.1 | 7.7 | 7.4 | 82 |
| *$A_0$ 1″—0″ | 33.6** | 19.6 | 7.6 | 12.0 | 87 |
| $B_{21}$ | 24.9 | 15.1 | 6.9 | 8.4 | 86 |

*72 hours' hydrolysis
**0.7 per cent of this reduction = loss if threonine and serine.

TABLE 2.—AMOUNTS OF MATERIALS USED

| | Weight taken | After methylation | Weight taken for $LiBH_4$ reduction | Per cent of N in solution after acid hydrolysis |
|---|---|---|---|---|
| | gm. | gm. | gm. | |
| $A_{00}$ (6″—3″) | 2.000 | 1.86 | 1.00 + 100 mgm. $LiBH_4$ in 20 ml. THF* | 79 |
| $A_0$ (3″—1″) | 2.000 | 1.79 | 1.00 + 100 mgm. $LiBH_4$ in 20 ml. THF* | 95 |
| $A_0$ (1″—0″) | 5.000 | 5.34 | 3.00 + 100 mgm. $LiBH_4$ in 25 ml. THF* | 86 |
| $B_{21}$ | 10.000 | 9.93 | 7.00 + 150 mgm. $LiBH_4$ in 30 ml. THF* | — |

*Tetrahydrofuran

## RESULTS AND DISCUSSION

Table 1 shows the nitrogen distribution in the hydrolyzates of the samples of the Cape Breton soil. The amounts of nitrogen accounted for as amino acid-N and as aspartic and glutamic acid-N are drawn from a previous report (15). If aspartic and glutamic acid were present in the soil as amides they would yield an amount of ammonia-N equal to their amino acid-N. When this figure is subtracted from the ammonia-N there is still a considerable amount of ammonia-N not accounted for. This increases with depth in the profile (or degree of decomposition) and with the length of time of hydrolysis. This suggests that some of the ammonia-N does not come from amide-N but from some other source [perhaps from products formed by the union of nitrogen with lignin degradation products (11) and from ammonia fixed by clay (8)].

Table 2 shows the pertinent data regarding amounts of samples and reagents used in the methylation and reduction procedures. These amounts of samples were chosen to give suitable aliquots for amino acid analysis.

The amounts of amino acids found in treated and untreated samples from the different horizons of the profile are shown in Table 3. In the $A_{00}$ layer (largely undecomposed leaf litter) there seems to be a loss of about

TABLE 3.—AMOUNTS OF AMINO ACIDS FORMED ON HYDROLYSIS OF CAPE BRETON SOIL BEFORE AND AFTER TREATMENT WITH $LiBH_4$
(expressed as mgm/gm. soil)

| | $A_{00}$ 6"—3" | | $A_0$ 3"—1" | | $A_0$ 1"—0" | | $B_{21}$ | |
|---|---|---|---|---|---|---|---|---|
| | *untreated | treated | *untreated | treated | *untreated | treated | *untreated | treated |
| Aspartic acid | 5.18 | 2.54 | 6.43 | 5.80 | 2.09 | 1.97 | 0.19 | 0.15 |
| Threonine | 3.40 | 1.89 | 3.83 | 3.81 | 1.37 | 1.35 | 0.09 | 0.09 |
| Serine | 3.27 | 1.98 | 3.97 | 3.35 | 1.37 | 1.13 | 0.07 | 0.09 |
| Glutamic acid | 6.06 | 3.34 | 6.93 | 5.30 | 2.28 | 1.88 | 0.20 | 0.18 |
| Proline | 2.83 | 2.40 | 2.97 | 2.75 | 0.99 | 1.02 | 0.06 | 0.06 |
| Glycine | 3.41 | 2.21 | 4.20 | 3.79 | 1.52 | 1.42 | 0.12 | 0.11 |
| Alanine | 3.48 | 2.65 | 4.36 | 4.02 | 1.41 | 1.38 | 0.09 | 0.12 |
| Valine | 3.66 | 2.49 | 3.56 | 3.11 | 1.36 | 1.05 | 0.09 | 0.09 |
| Cystine | 1.01 | — | 0.41 | — | 0.20 | — | 0.02 | — |
| Methionine | 0.58 | 0.32 | 0.51 | 0.26 | 0.23 | 0.12 | 0.01 | — |
| Isoleucine | 2.38 | 2.07 | 2.51 | 2.21 | 0.85 | 0.70 | 0.05 | 0.05 |
| Leucine | 4.08 | 2.91 | 3.48 | 3.27 | 1.31 | 1.15 | 0.08 | 0.08 |
| Tyrosine | 1.40 | 0.90 | 1.41 | 1.36 | 0.40 | 0.46 | 0.03 | 0.03 |
| Phenylalanine | 2.52 | 1.71 | 2.82 | 2.20 | 0.89 | 0.76 | 0.07 | 0.05 |

*See ref. 15

TABLE 4.—RATIOS OF AMINO ACID-N FORMED ON HYDROLYSIS OF CAPE BRETON SOIL BEFORE AND AFTER TREATMENT WITH $LiBH_4$
(Proline expressed as 100)

| | $A_{00}$ 6"—3" | | $A_0$ 3"—1" | | $A_0$ 1"—0" | | $B_{21}$ | |
|---|---|---|---|---|---|---|---|---|
| | untreated | treated | untreated | treated | untreated | treated | untreated | treated |
| Aspartic acid | 158 | 91 | 187 | 182 | 182 | 167 | 260 | 266 |
| Threonine | 116 | 76 | 125 | 134 | 134 | 128 | 137 | 140 |
| Serine | 127 | 90 | 147 | 133 | 152 | 122 | 122 | 124 |
| Glutamic acid | 167 | 109 | 183 | 151 | 181 | 144 | 250 | 240 |
| Proline | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Glycine | 185 | 141 | 217 | 211 | 235 | 213 | 299 | 280 |
| Alanine | 159 | 143 | 190 | 189 | 185 | 175 | 188 | 253 |
| Valine | 127 | 102 | 118 | 111 | 136 | 102 | 137 | 140 |
| Cystine | 34 | — | 13 | — | 19 | — | 28 | — |
| Methionine | 16 | 10 | 13 | 7 | 18 | 9 | 13 | — |
| Isoleucine | 74 | 76 | 74 | 70 | 76 | 60 | 72 | 77 |
| Leucine | 126 | 106 | 103 | 104 | 117 | 99 | 120 | 111 |
| Tyrosine | 31 | 24 | 30 | 31 | 26 | 29 | 30 | 31 |
| Phenylalanine | 62 | 50 | 66 | 56 | 63 | 52 | 83 | 84 |

20 to 45 per cent for most of the amino acids. The filtrates from the methylation and reduction treatments were not analysed for nitrogen, but it is hard to see how there could be so high a mechanical loss, especially since 79 per cent of the total-N was found in the hydrolyzate and there is no evidence of any such loss in the samples from the other horizons of the profile. On the other hand, it seems hardly more probable that the amino acids were combined in small peptides with free carboxyl groups to account for the loss, since this would mean that every fourth or fifth residue of most of the amino acids must exist at the end of the peptide chain with the carboxyl group free. Possibly both mechanical loss and reduction of free carboxyl groups may have caused this decrease. If so, it would seem that a considerable part of the amino acids of this material (the previous year's leaf-fall) must consist of relatively simple peptides. The percentage loss of glutamic and aspartic acids is apparently greater than that of most of the other amino acids; this may mean that part of these substances occurs as acids rather than entirely as amides. The amounts of amino acids in the treated and untreated samples from the other horizons of the profile do not seem to differ much more than experimental error, except possibly for glutamic acid.

Table 4 shows the ratios of the number of moles of the amino acids found in the different samples, with proline expressed as 100. Proline was taken as the reference acid since it is fairly easy to determine accurately and there is no evidence in the literature that it will be affected by the treatment unless it is at the end of a peptide chain with its carboxyl group free. Again there seems to be no evidence of very great differences in the amino acid distribution on treatment except in the case of the $A_{00}$ sample. The reduction in the amount of glutamic acid in the two $A_0$ samples may be somewhat greater than experimental error; this may mean that some of this acid is present in these samples as the acid rather than the amide.

Since the results of the $LiBH_4$ reduction work indicated that most of the glutamic and aspartic acids in soils were probably present as amides, it seemed of interest to estimate the amount of amide-N present in soil materials, for which adequate data on the contents of these acids were available, by some of the methods reported in the literature for determining amide-N. The method of Levy *et al.* was followed as outlined (9) except that the sample was washed into the flask with 30 ml. of 10 per cent NaOH. With this method the recovery of amide-N from acetamide, glutamine and alanyl asparagine was nearly 100 per cent; the yield from asparagine was somewhat low. These yields were not increased significantly by distilling for 10 minutes. With the method of Newton and Abraham (13) the diffusion time had to be lengthened to 24 to 48 hours to get near theoretical recoveries from the above materials. With soil materials 48-hour diffusion periods were used. The results are shown in Table 5. The data for glutamic and aspartic acid-N were calculated from results previously published (15); if these acids occurred entirely as amides, the amide-N should equal these values. Some of these results, especially those from samples of the lower horizon, were much too high. The diffusion method was time-consuming and the duplication of results with it was poor; hence not all the samples were analysed by this method. It is known that clay minerals fix ammonia that can be released by alkali and that the presence

TABLE 5.—APPARENT AMIDE CONTENT OF VARIOUS SOIL MATERIALS

| Soil material | Total-N % | Glutamic & aspartic -N % | NaOH amide-N % | | KOH amide-N % | | Metaborate amide-N % | |
|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 1 | 2 | 1 | 2 |
| *Podzol (Cape Breton, unnamed)* | | | | | | | | |
| $A_{00}$ 6–3 in. | 1.22 | 0.112 | 0.103 | 0.090 | — | — | 0.111 | 0.147 |
| $A_0$ 3–1 in. | 1.40 | 0.134 | 0.135 | 0.143 | 0.140 | 0.160 | 0.185 | 0.178 |
| $A_0$ 1–0 in. | 0.56 | 0.044 | 0.063 | 0.065 | — | — | 0.054 | 0.051 |
| $B_{21}$ 8–22 in. | 0.056 | 0.004 | 0.005 | 0.006 | 0.006 | 0.008 | 0.006 | 0.005 |
| *Podzol (Lydgate series)* | | | | | | | | |
| $A_0$ 6–4 in. | 2.28 | 0.160 | 0.170 | 0.185 | 0.180 | 0.190 | 0.20 | 0.20 |
| $B_{21}$ 4–6 in. | 0.285 | 0.15 | 0.030 | 0.031 | — | — | 0.032 | 0.032 |
| *Podzol (Port Hebert series)* | | | | | | | | |
| $A_0$ 10–0 in. | 0.954 | 0.050 | 0.111 | 0.111 | — | — | — | — |
| B 4–6 in. | 0.421 | 0.025 | 0.047 | 0.049 | 0.050 | 0.060 | — | — |
| *Black Solonetz (Morris series)* | | | | | | | | |
| A 0–1½ in. | 0.680 | 0.052 | 0.056 | 0.058 | 0.050 | 0.060 | — | — |
| B 14–18 in. | 0.228 | 0.011 | 0.022 | 0.018 | — | — | — | — |
| *Lennoxville humate* | 2.41 | 0.125 | 0.327 | 0.363 | 0.390 | 0.510 | 0.310 | 0.350 |
| *Lacombe humate* | 1.76 | 0.039 | 0.202 | 0.198 | 0.210 | 0.340 | 0.180 | 0.190 |

of K ion inhibits this release (8). Hence some of the samples were analysed using 2.5 N KOH instead of NaOH. The results were no lower and were harder to duplicate, due perhaps to the excessive foaming during steam distillation when KOH was used. No apparent correlation existed between the amount of clay in any of the samples and the amount of "excess" amide-N found. This "excess" amide-N was relatively no greater with the Lennoxville humate which contained illite and mixed layer 2:1 silicates than with the Lacombe humate which contained montmorillonite predominantly, although we could expect the former to fix more ammonia. None of the methods, apparently, gave satisfactory results, except with the $A_0$ or $A_{00}$ horizons where the organic material had not decomposed to a very great degree. The amount of "excess" ammonia-N formed by acid hydrolysis was also higher in lower horizons of the profile.

## CONCLUSIONS

Since this work was completed Chibnall and co-workers have reported in more detail on the use of the $LiBH_4$ method to estimate the amount of glutamine and asparagine in proteins (4). This work leaves no doubt that there are small errors in the method, i.e. loss of amide-N and some splitting of the peptide chain during methylation and reduction. However, these errors would not seriously affect the results reported here. Wilcox *et al.* (16) have also made a very recent study of the method to determine the amides of $\alpha$-chymotrypsinogen. Their work shows that, while the method leaves something to be desired, the errors found in the work on pure proteins are small. In the application of this method to soil materials a much more serious question is whether the carboxyl groups of aspartic and glutamic acids, if present, are susceptible to methylation or are blocked by something other than the amide group. There is no apparent way at present to resolve this difficulty. However, the extensive loss of amino acids from the $A_{00}$ sample and the changes in the amino acid ratios found to some extent on each of the samples may be taken as an indication that soil organic matter is not inert to the methylation and reduction treatments. Also the amide-N of slightly decomposed materials ($A_0$ horizons where ammonia absorbed on clay or combined in decomposed material would not be present) when determined by entirely different methods is approximately equal to the glutamic and aspartic acid-N. This supports the conclusion that glutamic and aspartic acids occur in soil largely as their amides.

Even if all the aspartic and glutamic acids are present in soil organic matter as amides, a considerable fraction of the ammonia-N formed by acid hydrolysis is still not accounted for. This increases with the degree of decomposition of the organic material and amounts to more than half in the lower part of the $A_0$ and in the B horizons. It also increases sharply with longer hydrolysis. Mattson and Koutler-Andersson have suggested that lignin degradation products may combine with ammonia to form soil organic matter (11) and many years ago Maillard (10) proposed the theory that humus was formed by reactions between sugars and amino acids and related compounds. The ammonia formed on acid hydrolysis

that is not derived from amides may have originated from materials formed by reactions of the above types and perhaps from ammonia fixed by clay; however, tropical soils oxidized to remove organic matter gave only traces of ammonia on hydrolysis with boiling acid or alkali (14). The formation of the nitrogenous components of humus would seem to be more complex than a simple lignin-protein interaction, especially in view of the fact that the more decomposed humus materials are lower in amino-N and higher in ammonia-N than less decomposed materials.

## ACKNOWLEDGEMENT

The writer wishes to acknowledge the assistance of R. J. Mott and O. E. Acres in portions of this work.

## REFERENCES

1. Bailey, J. L. The reduction of esters of simple peptides by metal hydrides. Biochem. J. 60: 170–173. 1955.
2. Bailey, J. L. Systematic degradation of peptides from the carboxyl end. Biochem. J. 60: 173–176. 1955.
3. Chibnall, A. C., and M. W. Rees. Identification and estimation of the amide and C-terminal residues in insulin by reduction of the ester with lithium borohydride. Ciba "Symposium on the chemical structure of proteins", pp. 70-81. J. and A. Churchill, Ltd., London. 1953.
4. Chibnall, A. C., and co-workers. Studies on the amide and C-terminal residues in proteins: 1, 2, 3, 5. Biochem. J. 68: 105-118, 122-128. 1958.
5. Crawhill, J. C., and D. F. Elliott. A search for specific chemical methods for fission of peptide bonds. II. Experiments involving reduction of C-terminal residues. Biochem. J. 61: 264-275. 1955.
6. Fromageot, C., and M. Jutisz. Identification of C-end groups in protein by reduction with lithium aluminum hydride. Ciba "Symposium on the chemical structure of proteins", pp. 82-97. J. and A. Churchill, Ltd., London. 1953.
7. Fromageot, C., M. Jutisz, D. Meyer, and L. Pénasse. Méthode pour la caractérization des groupes carboxyliques terminaux dans les protéines. Application à l'insuline. Biochem. Biophys. Acta 6: 283–289. 1950.
8. Hanway, J. J., A. D. Scott, and G. Stanford. Replaceability of ammonia fixed in clay minerals as influenced by ammonium or potassium in the extracting solution. Soil Sci. Soc. Amer. Proc. 21: 29-34. 1957.
9. Levy, A. L., I. I. Geschwind, and C. H. Li. Corticotropins (ACTH) II. Amino acid composition of α-corticotropin. J. Biol. Chem. 213: 187-196. 1955.
10. Maillard, L. C. Identité des matières humiques de synthèse avec les matières humiques naturelles. Ann. de Chimie. 9e série, 7: 113–152. 1917.
11. Mattson, S., and E. Koutler-Andersson. The acid-base condition in vegetation, litter and humus. VI. Ammonia fixation and humus nitrogen. Ann. Roy. Agr. Coll. Sweden 11: 107–134. 1943.
12. Mommaerts, W. F. H. M., and H. Neurath. Insulin methyl ester 1. Preparation and properties. J. Biol. Chem. 185: 909-917. 1950.
13. Newton, G. G. F., and E. P. Abraham. Observations on the nature of bacitracin A. Biochem. J. 53: 604–613. 1953.
14. Rodrigues, G. Fixed ammonia in tropical soils. J. Soil Sci. 5: 264–274. 1954.
15. Sowden, F. J. Distribution of amino acids in selected horizons of soil profiles. Soil Sci. 82: 491–496. 1956.
16. Wilcox, P. E., E. Cohen, and W. Tan. Amino acid composition of α-chymotrypsinogen including estimation of asparagine and glutamine. J. Biol. Chem. 228: 999–1019. 1957.

# MINERALOGICAL ANALYSIS OF THE SOILS OF THE MARITIME PROVINCES[1]

J. E. BRYDON

*Canada Department of Agriculture, Ottawa, Ontario*

[Received for publication April 3, 1958]

## ABSTRACT

The mineralogy of the clay and coarse silt fractions of 31 Maritime soils with a few exceptions showed close similarities. The predominant clay mineral was illite and it was associated with chlorite, vermiculite and kaolinite. Significant amounts of montmorillonite occurred in only one soil, the Truro. Vermiculite appeared in all the surface soil clays, and mixed-layer assemblages of various 2:1 layer silicates, including chloritic components, were present in many of the clays.

The silt fractions of the Nova Scotia and New Brunswick soils contained substantial amounts of albite-type plagioclase feldspar in addition to quartz, chlorite and mica. The Prince Edward Island soils, except the Queens, differed in that they contained small amounts of a variety of feldspars.

## INTRODUCTION

Investigation of the dikeland soils of the upper Bay of Fundy area of Nova Scotia (3) showed that the clay fractions consisted of illite, chlorite, kaolinite and montmorillonite. Subsequently, samples of four soil series of the adjoining uplands were examined in order to determine the nature of their clay minerals. These soils (Pugwash, Queens, Tormentine and Nappan), which were developed from glacial till overlying rocks of Carboniferous age, appeared to have the same clay mineralogy as the dikeland soils. According to the Soil Survey Reports (1, 12) the glacial till and the soil developed from it are related in most instances to the underlying rocks. Little pertinent information is available regarding the mineralogy of the soils, the tills, or the underlying rock formations. Since the similarity of the clays from the four upland soils and the dikeland soils had been demonstrated, the work reported here was initiated to determine gross variations in the mineralogy of soils in the three Maritime Provinces.

In selecting the soils, particular attention was paid to the assumed geological origin in order that a wide range of rock types and ages would be represented. Such a wide range would be expected to give maximum variations in mineralogy of the soils if the underlying rock formations were, in fact, the parent materials of the soils. There are extensive areas of igneous, metamorphic and sedimentary rocks of various ages back to Precambrian, most of which have been glaciated.

The soils are all in the Podzol Zone and descriptions of most of them have been given in the Soil Survey Reports of the area (1, 4, 5, 6, 8, 9, 11, 12, 13, 14). Since the objective was to determine whether the mineralogy varied qualitatively between the soil series, only one sample was taken from each profile. Composite samples of cultivated surface soils from Nova Scotia and samples of the C horizon of the New Brunswick and Prince Edward Island soils were taken for the investigation.

[1] Contribution No. 393, Chemistry Division, Science Service, Canada Department of Agriculture, Ottawa, Ont.

TABLE 1.—MINERALOGY OF THE SELECTED SOILS FROM THE MARITIME PROVINCES

| Soil type | Underlying rock | | Location | Silt mineralogy | | | Clay mineralogy | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Age | Type | | High | Low | Trace | I. | C. | V. | K. | Mo. | M-L |
| *Nova Scotia* | | | | | | | | | | | | |
| Yarmouth | Precambrian | Hornblendeschist | Hebron, Yarmouth Co. | F,C,M,H | Q | | * | * | * | tr | tr | * |
| Halifax | Precambrian | Quartzite, slate | Waverly, Halifax Co. | Q,F | C,M | | * | * | * | * | | * * * |
| Cobequid I | Precambrian | Granite | Nuttby, Colchester Co. | Q | F,C,M | | * | tr | * | tr | tr | |
| Cobequid II | Precambrian | Granite | Dalhousie Mtn., Pictou Co. | Q | F,C | M | * | * | * | tr | | * * |
| Barney | Silurian | Shales | French River, Pictou Co. | Q,F | C,M | | * | | * | * | | |
| Gibraltar | Devonian | Biotite granite | Shelbourne, Shelbourne Co. | Q,F | C,M | | * | | * | * | tr | * |
| Diligence | Carboniferous | Shales | East Mountain, Colchester Co. | Q | F,C,M | | * | tr | * | tr | tr | * * * |
| Queens | Carboniferous | Shales | Stewiacke East, Colchester Co. | Q | F,M | C | * | * | * | * | | |
| Merigomish | Carboniferous | Sandstone | Merigomish, Pictou Co. | Q | F | C,M | * | tr | * | * | tr | |
| Shulie | Carboniferous | Sandstone | Riversdale, Colchester Co. | Q | F,C,M | | * | | * | | tr | |
| Westbrook | Carboniferous | Conglomerate | Green Hill, Pictou Co. | Q,F | | C,M | * | * | * | tr | tr | * * |
| Truro | Triassic | Sandstone | Belmont, Colchester Co. | Q | F,C,M | | * | * | * | * | * | |
| *New Brunswick* | | | | | | | | | | | | |
| Caribou | Silurian | Shales, slates, s.s. | Ennishore, Victoria Co. | Q | F,C,M | | * | * | tr | * | | |
| Jardine S | Silurian | Shales, slates, s.s. | St. Quentin, Restigouche Co. | Q,F | C,M | | * | * | | tr | | * |
| Jardine D | Silurian | Shales, slates, s.s. | St. Quentin, Restigouche Co. | Q,F | C,M | | * | * | | tr | | |
| Violette | Silurian | Shales, slates | Dube, Madawaska Co. | C,F | Q,M | | * | * | | | | |
| Glassville | Silurian | Shales, slates | McKee Brook, Victoria Co. | Q,F | C,M | | * | * | | tr | | |
| Holmesville | Silurian | Shales, slates | California Sett., Victoria Co. | Q,F | C,M | H | * | * | * | * | tr | |
| Seigas | Silurian | Shales, slates, s.s. | St. Leonard, Madawaska Co. | Q | F,C,M | H | * | | * | * | | * * |
| Juniper | Lower Devonian | Mixed igneous | Juniper, Carleton Co. | Q | F,C | M | * | * | tr | tr | | * |
| Canterbury | Silurian & older | Mixed | Queenston, Queens Co. | Q | C,M | F | * | | | * | | |
| Tormentine | Carboniferous | S.s. | Midgic, Westmorland Co. | Q,F | C,M | | * | * | tr | * | | |
| Queens | Carboniferous | S.s., mudstone | Fredericton, York Co. | Q | F | C,M | * | tr | | * | | |
| Fundy | Recent | Marine sediments | Milltown, Charlotte Co. | Q | F,C,M | | * | * | tr | * | | |
| *Prince Edward Island* | | | | | | | | | | | | |
| Charlottetown | Carboniferous | S.s. | Charlottetown, Queens Co. | Q | F,C,M | | * | * | | * | | |
| O'Leary | Carboniferous | S.s. | O'Leary Sta., Prince Co. | Q | F,C,M | | * | * | | * | | |
| Alberry | Carboniferous | S.s. | Montague, Kings Co. | Q | C,M | | * | * | | * | | * |
| Culloden | Carboniferous | S.s. | Lower Montague, Kings Co. | Q | C,M | | * | * | tr | * | tr | |
| Armadale | Carboniferous | S.s. | Midgell River, Kings Co. | Q | C,M | F | * | * | tr | * | tr | |
| Queens | Carboniferous | S.s. | Vernon, Queens Co. | Q,F | C,M | | * | * | tr | * | tr | |
| Kildare | Recent | Marine sand | Tignish, Prince Co. | Q | F | M | * | * | | tr | tr | * |

Q— quartz; F— feldspar (albite); C— chlorite; M— mica; H— hornblende; I— Illite; V— Vermiculite; K— Kaolinite; *Present in significant amounts.
Mo— montmorillonite; M-L— mixed layer minerals; Tr— Trace. s.s.— sandstone.

## EXPERIMENTAL METHODS

Twenty-gram samples of each soil were treated with $H_2O_2$ where necessary to remove organic matter. They were then acidified with HCl to pH 3.5, washed by centrifuging, and titrated to pH 8 with NaOH. The <1.4 micron fraction was separated by a 16-hour sedimentation procedure. The 50-20 micron silt fraction was recovered by repeated sedimentations to remove <20 micron material, and by sieving the remaining sediment to remove >50 micron sand.

Non-oriented, ground coarse silt specimens and oriented clay specimens were examined with a Norelco x-ray diffractometer using Fe-filtered Co radiation. The oriented specimens were prepared by air-drying some of the <1.4 micron clay suspension on glass slides. Diffraction patterns of the clays were obtained in the air-dry state, after glycolation and after heating for 1 hour at 400° C.

## RESULTS

Table 1 lists the Nova Scotia, New Brunswick and Prince Edward Island soils and shows their location, underlying geological formation or, in the case of the Fundy and Kildare soils, the origin of the soil material. The mineralogy of the coarse silt fraction and the <1.4 micron clay fraction is included.

### *Coarse Silt Fraction*

The silt mineralogy varied somewhat from soil to soil but the differences were not large. The Yarmouth and Violette soils were unique in having weak quartz patterns, while in the remainder the quartz pattern was strong. Both the Yarmouth and Violette had medium strong plagioclase feldspar and chlorite peaks and, while the Violette had weak mica peaks, the Yarmouth sample gave medium strong mica peaks, and, in addition, medium strong hornblende peaks.

All of the Nova Scotia and New Brunswick soils, except the poorly-drained Canterbury, gave medium to strong plagioclase feldspar patterns. The Queens from Prince Edward Island differed from the other Prince Edward Island soils and resembled those on the mainland in having a strong plagioclase feldspar pattern. In the other Prince Edward Island soils, the plagioclase reflections were weak (Charlottetown, O'Leary, Armadale, Kildare) or absent (Alberry, Culloden). In all but three cases the feldspar patterns corresponded to those of the albite end of the plagioclase series. However, in three of the Prince Edward Island soils (Alberry, Culloden and Armadale), there was some evidence that Ca or K feldspars may have been present. Thus, in the mainland soils the feldspars were predominantly albite-type, whereas the Prince Edward Island soils contained a variety of, and smaller amounts of, feldspars.

Except for the Yarmouth and Violette soils and the feldspar differences between Prince Edward Island and mainland soils, no large variations in mineralogy were shown. Weak mica reflections were shown by all samples and chlorite reflections were present in all samples except the Kildare sand of marine origin in Prince Edward Island. There was some indication that hornblende may have been present in small amounts in the Holmesville and Seigas silts.

*Clay Fraction*

With few exceptions the soils fell into two general groups on the basis of clay mineralogy. The clays from the Nova Scotia surface soils and from three of the New Brunswick C horizons (Jardine S, Seigas, Juniper) gave weak illite and weak vermiculite diffraction peaks. The remainder of the clays gave strong illite peaks with a significant chlorite peak rather than vermiculite. All clays appeared to contain small amounts of kaolinite.

All of the Nova Scotia soils, except Barney and Shulie, had random-mixed-layering, the latter two consisting primarily of illite and vermiculite with traces of montmorillonite. Of all the Maritime soils the Truro sample was unique in having a significant content of montmorillonite. Whereas most of the New Brunswick and Prince Edward Island soil clays produced strong illite reflections, those which did not (Seigas, Jardine S, Juniper) showed evidence of mixed-layering. Similarly, while most of the New Brunswick and Prince Edward Island clays gave weak though definite chlorite peaks, those which did not had mixed-layers with chloritic components. The poorly-drained Canterbury was the only clay containing no chloritic component.

## DISCUSSION

From the results, it is apparent that there was generally no large difference in mineralogy between soils overlying different geological formations. The exceptions were the Yarmouth and Truro soils in Nova Scotia and the Prince Edward Island soils except the Queens. The Yarmouth overlying a hornblende schist contained significant amounts of hornblende in the coarse silt fraction. The Truro, which was the only soil overlying Triassic sandstones, was unique in giving a measurable montmorillonite peak.

The Prince Edward Island soils, except the Queens, differed from those on the mainland on the basis of silt mineralogy. They consisted of a mixture of feldspars in small amounts, whereas the mainland silt fractions gave medium to strong albite-type plagioclase feldspar peaks. The Queens from Prince Edward Island is related to the mainland soils in having a strong plagioclase feldspar pattern. This is in agreement with Whiteside's observation (11) that the Queens in Prince Edward Island was developed from till which was similar to the material found in the Cumberland plain in Nova Scotia and which had been deposited in depths from 2 to 10 feet over the red till common to the Island.

It might be expected that the mineralogy of soils overlying Carboniferous and Silurian shales, sandstones and mudstones would be rather similar. However, it is surprising that there were few important differences in mineralogy related to known geological formations.

There are several reasons which may be advanced to account for the similarity of the mineralogy in different soils. The mixing of the soil material by glacial action may have been much more efficient than is generally recognized (1, 12), the mineralogy of the underlying rocks may have been qualitatively similar, or weathering of certain minerals may have eliminated major differences in the soils.

Some generalizations regarding weathering of minerals in the Maritime soils are suggested on the basis of these results. The patterns of the surface soil clays, and those of a few of the C horizons were weak and showed mixed-layering of 2:1 layer silicates in addition to vermiculite. The presence of vermiculite in the surface soils leads to the suggestion that it was the weathering product in the area, and possibly that it was the alteration product of illite- and chlorite-rich clays as has been found in New England soils (2, 10). Detailed profile studies are necessary to resolve these relationships conclusively.

While alteration of the minerals in the clay fraction appears to have taken place, the presence of albite-type plagioclase feldspar in the coarse silt fraction of the surface soils would indicate that weathering has not been too drastic. Albite is generally recognized as being moderately susceptible to alteration according to proposed weathering sequences, and yet it appears to persist in the surface soils under the strong podzolic weathering regime characteristic of the region.

In summary, the results show:

(1) that the coarse silt fractions of the Maritime soils consist of quartz, plagioclase feldspar, chlorite and mica in varying proportions;

(2) that the clay fractions consist predominantly of illite with lesser amounts of chlorite, kaolinite and vermiculite;

(3) that montmorillonite is generally a minor constituent;

(4) that the Prince Edward Island soils have slightly different mineralogy than those on the mainland; and

(5) that there are few definite relationships of mineralogy with known geological formations.

## ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of D. B. Cann, J. F. G. Millette and J. R. Wright in supplying the soil samples investigated in this report.

## REFERENCES

1. Aalund, H., and R. E. Wicklund. Soil survey report of Southeastern New Brunswick. 3rd Rept., N. B. Soil Survey. 1950.
2. Bourbeau, G. A., and C. L. W. Swanson. The morphology, mineralogy and genesis of two southern New England soils. Conn. Agr. Expt. Sta. Bull. 584. 1954.
3. Brydon, J. E., and H. Heystek. A mineralogical and chemical study of the dikeland soils of Nova Scotia. Can J. Soil Sci. 38: 171-185. 1958.
4. Cann, D. B., and R. E. Wicklund. Soil survey of Pictou County, Nova Scotia. Rept. No. 4, N. S. Soil Survey. 1950.
5. Cann, D. B., and J. D. Hilchey. Soil survey of Antigonish County, Nova Scotia. Rept. No. 6, N. S. Soil Survey. 1954.
6. Cann, D. B., J. D. Hilchey, and G. R. Smith. Soil survey of Hants County, Nova Scotia. Rept. No. 5, N. S. Soil Survey. 1954.
7. Krebs, R. D., and J. C. F. Tedrow. Genesis of three soils derived from Wisconsin till in New Jersey. Soil Sci. 83: 207-218. 1957.
8. Stobbe, P. C. Soil survey of the Fredericton-Gagetown area of New Brunswick. 1st Rept., N. B. Soil Survey. Pub. 709, Can. Dept. Agr. 1940.

9. Stobbe, P. C., and H. Aalund. Soil survey of the Woodstock Area, New Brunswick. 2nd Rept., N. B. Soil Survey. Pub. 757, Can. Dept. Agr. 1944.
10. Tamura, Tsuneo. Physical, chemical and mineralogical properties of Brown Podzolic soils in Southern New England. Soil Sci. 81: 287-299. 1956.
11. Whiteside, G. B. Soil survey of Prince Edward Island. Charlottetown. 1950.
12. Whiteside, G. B., R. E. Wicklund, and G. R. Smith. Soil survey of Cumberland County, Nova Scotia. Rept. 2, N. S. Soil Survey. 1945.
13. Wicklund, R. E., and G. R. Smith. Soil survey of Colchester Co., Nova Scotia. Rept. No. 3, N. S. Soil Survey. 1948.
14. Wicklund, R. E., and K. K. Langmaid. Soil survey of southwestern New Brunswick. 4th Rept., N. B. Soil Survey. 1953.

# MEASUREMENT OF NITRATE-SUPPLYING POWER OF SOILS BY AN INCUBATION METHOD AND CORRELATION WITH CROP YIELD RESPONSE[1]

D. J. EAGLE AND B. C. MATTHEWS[2]

*Ontario Agricultural College, Guelph, Ontario*

[Received for publication May 12, 1958]

## ABSTRACT

The results of an incubation method for measuring the capacity of Ontario soils to accumulate nitrate were extremely variable. Placement of the soil sample between two layers of vermiculite in the incubation tube and addition of sufficient distilled water to moisten the top layer of vermiculite, the soil and a portion of the bottom layer of vermiculite resulted in satisfactory reproducibility of results. Wide fluctuations in results, due to prolonged air-dry storage before analysis or to time of sampling during the growing season, were reduced by storing all samples in the moist state at 10° C. for 2 weeks before analysis.

The correlation between the logarithm of the percentage yield decrement, which is a measure of crop response, and nitrate-supplying power as measured by the modified incubation method was highly significant for winter wheat ($r = -0.437$), oats ($r = -0.411$) and potatoes ($r = -0.651$). Soils having a nitrate-supplying power of 50 p.p.m. of N or more by the proposed modified method gave little or no increase in yield of wheat, oats, or potatoes when additional nitrogen was applied as fertilizer.

## INTRODUCTION

The inorganic nitrogen content of soil fluctuates widely over short periods of time due to variations in soil temperature and moisture, plant growth and fertilization. Although the organic nitrogen content, which makes up about 99 per cent of the total nitrogen in soil, is relatively constant, the total organic nitrogen in soil is of less significance than the rate of change of organic nitrogen to forms that may be absorbed by plant roots. It may be expected, therefore, that the rate of change of organic nitrogen to nitrate nitrogen, i.e. nitrate-supplying power, is the major soil characteristic that will correlate with the capacity of soil to supply nitrogen to crops. Nitrate-supplying power of soil depends on biological processes which are affected by such factors as nutrient supply, soil pH, carbon: nitrogen ratio, and aeration. Laboratory incubation procedures have been proposed to measure the nitrate-supplying power of soil (6, 8, 10, 11).

The incubation method recently proposed by Stanford and Hanway (11) has been shown to provide results that correlate well with crop response to nitrogen fertilization in field and greenhouse tests in Iowa (7, 9). Cook *et al.* (5) showed that the results of the incubation procedure as proposed by Stanford and Hanway were closely correlated with yield response and uptake of nitrogen by wheat on several soils in Saskatchewan. Saunder *et al.* (10) have recently reported satisfactory results by an incubation procedure for estimating the available nitrogen of soils in Southern Rhodesia.

[1]Contribution from Department of Soils, Ontario Agricultural College, Guelph, Ontario. Part of thesis presented by the senior author to the Graduate School, University of Toronto, in partial fulfilment of requirements for M.S.A. degree.

[2]Laboratory Scientist and Professor of Soils, respectively.

The objectives of this study were: (a) to evaluate the factors affecting the results of the incubation method for measuring the nitrate-supplying power of Ontario soils, and (b) to determine the degree of correlation between nitrate-supplying power of soils and yield of crops grown on the soils in the field.

## FACTORS AFFECTING THE RESULTS OF THE INCUBATION METHOD

Initially, the incubation method for measuring nitrate-supplying power of soils was used as described by Stanford and Hanway (11). It was found, however, that the results were extremely variable. The average variability among replicate determinations was 37 per cent for the 16 soils included in this preliminary evaluation. It was also found that the use of 60 ml. of distilled water, as recommended by Stanford and Hanway (11), to leach the nitrate from the soil samples before and after incubation was insufficient to effect quantitative removal of the nitrate. A total of 100 ml. of distilled water, in 10 ml.-aliquots, however, did completely remove the nitrates from the soil samples.

It was not possible in this laboratory to achieve the recommended suction of 0.4 to 0.7 atmosphere to adjust the moisture content of the soil samples before incubation. Indeed with the medium to coarse textured soils, the maximum suction attained was usually less than 0.2 atmosphere. Moreover, the amount of suction attained varied among replicates of the same sample presumably because of variations in the degree of compaction of the soil-vermiculite mixture in the incubation tube. At the same time the moisture content of the soil samples following the suction treatment was found to vary widely even among replicates of the same soil.

### *Moisture Adjustment in Soil Samples Before Incubation*

The inadequate control of the amount of suction applied could have caused variations in porosity, and hence aeration, of the samples during incubation. On the other hand, it seemed more likely that variations in moisture content caused by differences in suction were the primary cause of the variability in the amount of nitrate accumulated during incubation. Hence a new technique was devised for moisture adjustment in the soil samples.

TABLE 1.—MOISTURE CONTENT OF SOILS IN INCUBATION TUBES AFTER DIFFERENT PERIODS OF INCUBATION

| Soil type | Moisture content (per cent of oven-dry weight) after incubation periods of: | | | | | |
|---|---|---|---|---|---|---|
| | 2 hr. | 6 hr. | 1 day | 2 days | 7 days | 14 days |
| Haldimand clay | 31.7 | 28.4 | 27.6 | 25.9 | 25.7 | 25.1 |
| Brookston clay loam | 31.2 | 28.6 | 26.7 | 25.9 | 25.8 | 25.5 |
| Fox sandy loam | 16.9 | 14.8 | 13.3 | 13.3 | 13.0 | 12.8 |

TABLE 2.—MOISTURE EQUIVALENT AND MOISTURE CONTENT OF SOILS IN INCUBATION TUBES AFTER INCUBATION FOR 2 DAYS

| Soil type | Soil moisture content (per cent of oven-dry weight) | |
|---|---|---|
| | Moisture equivalent | Moisture content in equilibrium with dry vermiculite |
| Malton clay | 26.1 | 23.7 |
| Brookston clay loam | 29.3 | 25.9 |
| Haldimand clay loam | 24.3 | 21.5 |
| Schomberg silty clay loam | 27.3 | 24.2 |
| Harriston silt loam | 26.4 | 23.8 |
| Listowel silt loam | 25.7 | 21.9 |
| Burford loam | 18.2 | 16.0 |
| Fox sandy loam | 15.6 | 14.3 |
| Tioga loamy sand | 8.2 | 7.0 |
| Mean | 22.3 | 19.8 |

Powdered vermiculite, to a depth of 3 centimetres, was placed in a cylindrical plastic tube, 90 mm. long and 25 mm. in diameter, with a small hole in the bottom and in the cap. A 10-gm. sample of air-dry soil was placed on top of the vermiculite and a second layer of vermiculite was placed on top of the soil sample. Soil and vermiculite were not intermixed. Distilled water, approximately 7 ml., was added to wet the upper layer of vermiculite, the soil and the upper portion of the lower layer of vermiculite.

The moisture contents of replicates of the same soil treated in this way were found to be almost constant. The moisture content of the samples did decrease during the initial stages of incubation as shown for three representative soils in Table 1. However, after the first 2 days the moisture content reached a relatively constant value. The moisture content of samples of several soils at the end of a 2-day incubation period was found to approximate the moisture equivalent of the respective soils determined by the method of Briggs and McLane (3) as shown in Table 2. Several workers have found that a soil moisture content at or near moisture equivalent was most favourable for nitrification.

When the revised procedure for moisture adjustment was incorporated in the incubation method the variability among replicates was reduced to 6 per cent, compared to 37 per cent for the same soils by the original method. The nitrate initially present in the soil was determined on a separate sample and subtracted from the nitrate content after incubation to determine the nitrates accumulated during incubation.

*Effect of Length of Incubation Period*

The rate of accumulation of nitrate by several soil samples recently taken from the field and air-dried as measured by the modified incubation method is shown in Figure 1. In most cases there was a reduction in the rate of accumulation of nitrate during the second week of incubation com-

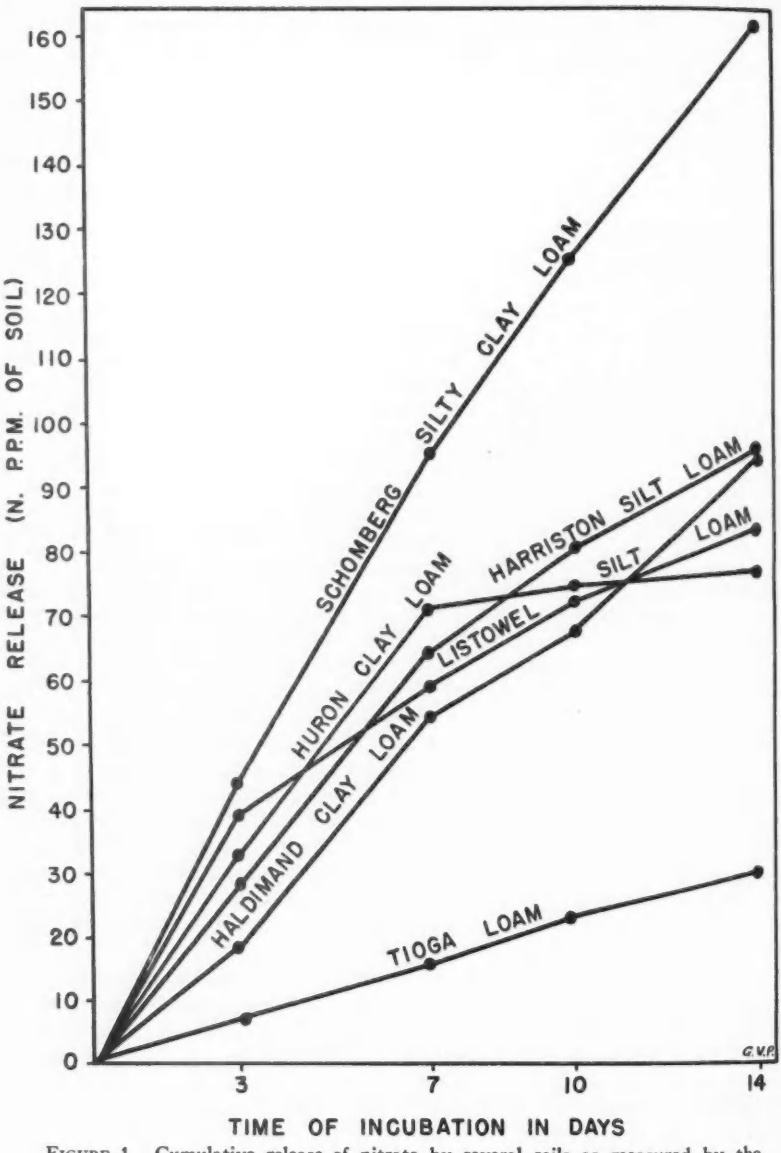



FIGURE 1. Cumulative release of nitrate by several soils as measured by the modified incubation method.

pared to the release during the first week. This reduction in rate was in general most evident for those soils having the highest rates of release of nitrate during the first week. Allison and Sterling (1) attributed a similar

TABLE 3.—EFFECT OF INITIAL NITRATE CONTENT OF SOIL ON NITRATE ACCUMULATION DURING 7-DAY INCUBATION BY MODIFIED INCUBATION METHOD

| Soil type | $NO_3$-N accumulated (p.p.m. of soil) with initial $NO_3$-N contents of: | | | | |
|---|---|---|---|---|---|
| | 0 p.p.m. | 20 p.p.m. | 40 p.p.m. | 70 p.p.m. | 100 p.p.m. |
| Fox sandy loam | 49 | 47 | 48 | 46 | 43 |
| Burford loam | 51 | — | 45 | 40 | — |
| Guelph loam | 92 | 95 | 93 | 91 | 84 |
| Huron clay loam | 91 | 90 | 91 | 90 | 82 |
| Brookston clay | 66 | 65 | 64 | 63 | 60 |

reduction in rate of nitrate formation, during prolonged incubation, to increasing acidity in the soil due to an increase in nitric acid content. At any rate, it was evident that a 7-day incubation period was adequate to evaluate the nitrate-supplying power of soils and the possible depressing effect of accumulated nitrate during a 14-day incubation could thus be avoided.

*Effect of Initial Nitrate Content on Nitrate Accumulated During Incubation*

Because the proposed procedure for moisture adjustment in the soil samples did not permit the removal of nitrates from the samples before incubation, it was necessary to determine the effect of initial nitrate content on the nitrate subsequently accumulated during incubation. Therefore, nitrate contents of 0, 20, 40, 70, and 100 p.p.m. of N were established in several soils by leaching with 100 ml. of distilled water and then adding the required amount of nitrate in solution as calcium nitrate. The soils were air-dried and analysed immediately by the incubation method using the revised procedure for moisture adjustment and a 7-day incubation period. The results for some representative soils, as shown in Table 3, indicate that the presence of nitrate in the soil in concentrations of 70 p.p.m. of N or more caused a depression in measured nitrate-supplying power. None of the soils used in this preliminary study or in the correlation study reported later contained more than 40 p.p.m. of N as nitrate initially.

*Effect of Date of Sampling and Length of Air-Dry Storage Period*

Several investigators (8, 12) have shown that the rate of release of organic nitrogen to inorganic form is influenced by cropping immediately prior to sampling. Starkey (12) concluded that the determination of nitrate-supplying power of soil during or immediately after the growth of plants was of no value because the surplus of fresh organic material with a high C:N ratio prevented normal release of nitrates by the soil. Moreover the microbial population in soil near actively growing roots apparently may be altered to the extent that the proportion of denitrifying bacteria relative to the nitrifying bacteria is increased (4).

The nitrate-supplying power of the Burford, Guelph, Fox and Haldimand soils as measured by the modified incubation method was not affected

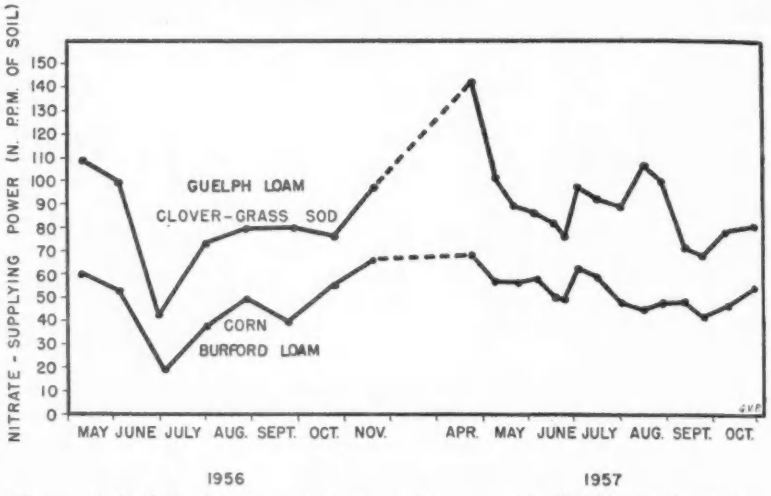



FIGURE 2. Variation in measured nitrate-supplying power of soils with date of sampling.

by air-drying of the soil provided the analyses were made immediately after drying. There was, however, some variation in test value with date of sampling as shown in Figure 2 for the Burford and Guelph soils. All samples were air-dried immediately before analysis. In 1956, the measured nitrate-supplying power reached a minimum for samples taken in early July and increased in samples taken later so that the November samples gave test values similar to those for the same soils sampled the previous May. In 1957, there was also a decline in test value with date of sampling from May to early July. Samples taken in late July and August gave relatively higher test values and a second minimum was measured for samples taken in late September.

Such variations in measured nitrate-supplying power with date of sampling precluded the use of the results as a basis for making fertilizer recommendations unless all samples were taken in May or November. It was found, however, that storage of the 1957 samples in the moist state at 10° C. for 2 weeks, reduced the variation in measured nitrate-supplying power due to date of sampling. The data in Table 4 show that a 14-day period of moist storage at 10° C. reduced the mean difference between the nitrate-supplying power of the samples taken on May 9 and the nitrate-supplying power of samples taken from the same plot area throughout the remainder of the growing season.

As stated previously, air-drying of the soil had a negligible effect on the measured nitrate-supplying power. However, prolonged storage of the air-dry samples before being tested did cause marked increases or decreases in nitrate-supplying power subsequently measured. Several workers (8) have found that storage of soil samples in the air-dry state resulted in a "partial sterilization effect", enhancing the rate of mineralization subsequently measured by incubation. The changes in nitrate-supplying

TABLE 4.—NITRATE PRODUCED DURING 7-DAY INCUBATION BY THREE SOILS IMMEDIATELY AFTER FIELD SAMPLING AND AFTER MOIST STORAGE AT 10° C.

| Sampling date | Nitrate produced (N p.p.m. of soil)* | | | | | |
|---|---|---|---|---|---|---|
| | Burford loam (corn cover) | | Guelph loam (clover-grass cover) | | Fox sandy loam (grass cover) | |
| | Storage period | | Storage period | | Storage period | |
| | 0 | 14 days | 0 | 14 days | 0 | 14 days |
| May 9 | 56 | | 100 | | 72 | |
| June 19 | 50 | 57 | 81 | 113 | 60 | 76 |
| June 26 | 49 | 65 | 74 | 108 | 57 | 77 |
| July 17 | | | 92 | 107 | 61 | 68 |
| July 31 | 47 | 58 | 87 | 102 | 56 | 71 |
| Aug. 14 | 45 | 58 | 106 | 95 | 62 | 70 |
| Aug. 28 | 47 | 57 | 100 | 95 | 72 | 73 |
| Sept. 11 | 47 | 52 | 71 | 91 | 59 | 61 |
| Sept. 25 | 42 | 45 | 67 | 66 | | |
| Oct. 9 | 46 | 52 | 77 | 82 | | |
| Oct. 31 | 55 | 60 | | | | |
| Mean difference of all values from May 9th value | 8.4 | 4.2 | 17.4 | 11.2 | 11.0 | 4.0 |
| Standard deviation | ±3.6 | ±3.5 | ±11.3 | ±9.7 | ±5.3 | ±3.5 |

*All samples were air-dried immediately before analysis.

TABLE 5.—CROPS, FERTILIZER TREATMENTS, NUMBER OF COMPARISONS AND NUMBER OF SOIL TYPES INCLUDED IN CORRELATION STUDY

| Crop | Fertilizer treatment | | | No. of comparisons | No. of soil types included |
|---|---|---|---|---|---|
| | N* | $P_2O_5$** | $K_2O$** | | |
| | lb./ac. | lb./ac. | lb./ac. | | |
| Winter wheat | 50 | 50 | 50 | 54 | 6 |
| Oats | 40 | 50 | 50 | 52 | 10 |
| Potatoes | 100 | 100 | 100 | 23 | 7 |

*Applied to fully treated plots only
**Applied to all plots

power of soils upon air-dry storage, i.e. storage beyond the 2 or 3 days required for air-drying, appeared to be unpredictable, as shown in Figure 3, for the Burford soil, in regard to extent or direction of the change. Similar results were obtained for Fox, Guelph and Haldimand soils. Several attempts to recondition samples, after air-dry storage, to attain a nitrate-supplying power similar to that determined from the samples immediately after air-drying were unsuccessful.

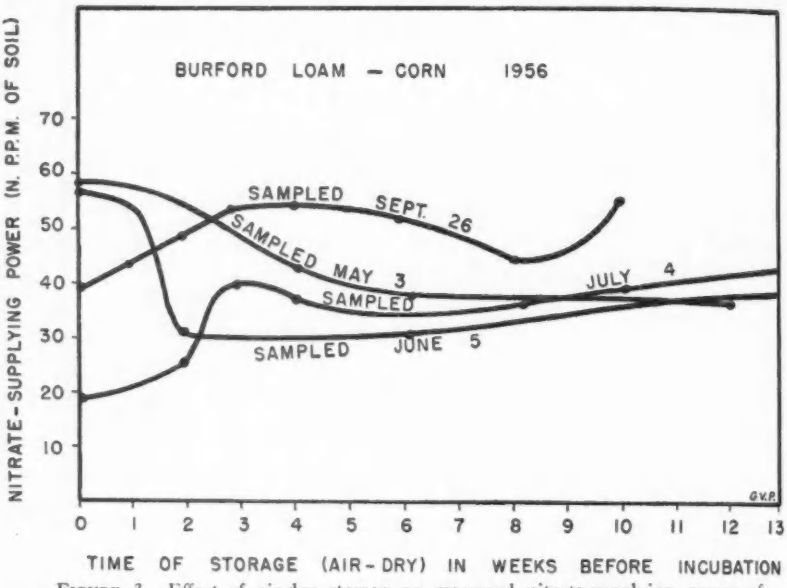



FIGURE 3. Effect of air-dry storage on measured nitrate-supplying power of Burford loam.

## MODIFIED INCUBATION METHOD

On the basis of the results reported, the incubation method of Stanford and Hanway was modified in several details. The description of the modified incubation method is reported here.

Soil samples were stored in the field moist condition at 10° C. for two weeks following sampling. Immediately before analysis the samples were air-dried and ground to pass through a 2-mm. sieve. Powdered vermiculite, to a depth of 3 centimetres, was placed in plastic tubes previously described. A 10-gm. sample of air-dry soil was placed on top of the vermiculite and a second layer of 3 centimetres of vermiculite was added on top of the soil. Distilled water, approximately 7 ml., was added to wet the upper layer of vermiculite, the soil and the upper portion of the lower layer of vermiculite. The soil was then incubated at 35° C. and high relative humidity for one week. After incubation the soil was leached with 100 ml. of distilled water in 10-ml. aliquots and nitrate was measured in the leachate by the phenoldisulphonic acid method. The initial nitrate content of the soil, determined by leaching a separate sample of the soil with 100 ml. of distilled water, was subtracted from the nitrate content after incubation to determine the nitrate accumulated during incubation.

## CORRELATION BETWEEN NITRATE-SUPPLYING POWER OF SOILS AS MEASURED BY MODIFIED INCUBATION METHOD AND YIELD OF CROPS IN THE FIELD

Because nitrates are completely soluble in the soil solution, Bray (2) considered nitrate nitrogen as a mobile nutrient. Hence yield of crop and soil nitrate content should be related by Liebig's Law of the Minimum.

Soil phosphorus and potassium, however, being relatively insoluble were considered to be immobile and therefore should be related to crop yield by the modified Mitscherlich equation as follows:

$$\text{Log } (100-y) = \text{Log } 100 - c_1 b \qquad (1)$$

where the yield on the fully fertilized plot = 100 per cent, y = percentage yield on the adjacent plot from which one fertilizer nutrient has been omitted, b = amount of the nutrient in the surface soil as measured by soil test and $c_1$ = a proportionality constant representing the efficiency per unit of the soil nutrient measured by the test.

The modified incubation method employed in this study, however, measured the nitrate-supplying power of soils and not the nitrate content of the soil at a particular time. It is, no doubt, true that an increase in the size of the root system for foraging does not increase the amount of nitrate capable of being absorbed from a given soil as it does the amount of phosphorus and potassium capable of being absorbed. On the other hand, factors such as temperature, moisture supply, and plant nutrients (other than nitrogen) that affect the size of plants, and hence crop yield, have a similar effect on microbial activity, and hence nitrate-supplying power. It is reasonable, therefore, to apply the percentage yield concept and the Mitscherlich equation as incorporated in equation 1 to relate the results of the modified incubation method to percentage yield of crop.

Yield data were obtained from field fertilizer tests conducted on privately-owned farms in the central and western parts of Southern Ontario for oats and potatoes in 1956 and 1957 and for wheat in 1957. The field plots were designed to provide comparisons between yields of plots receiving no nitrogen fertilizer and those receiving a full nitrogen treatment for calculation of percentage yields (y) in Equation 1. The crops, fertilizer treatments, number of comparisons and number of soil types involved in the correlation study are shown in Table 5.

A sample of the surface soil of each plot was taken before application of the fertilizer. The samples were air-dried, ground to pass through a 2-mm. sieve and the nitrate-supplying power was determined by the modified incubation method described previously.

The yield of crop without nitrogen fertilizer was calculated as a percentage of the yield with nitrogen fertilizer and substituted for y in equation 1 and the soil test value for the respective plot was substituted for b. The $c_1$ values were then calculated for each comparison.

TABLE 6.—STATISTICAL MEASUREMENTS OF DEGREE OF CORRELATION BETWEEN SOIL TEST VALUES FOR NITRATE-SUPPLYING POWER AND PERCENTAGE YIELD OF CROPS

| Crop | Coefficient of correlation (r) | Standard error of estimate (Sy) | $c_1$ values | |
|---|---|---|---|---|
| | | | Mean | Coefficient of variation (V) |
| | | % | | % |
| Wheat | −0.437** | 11.1 | 0.0182 | 43.9 |
| Oats | −0.411** | 11.6 | 0.0187 | 47.5 |
| Potatoes | −0.651** | 9.7 | 0.0233 | 34.7 |

**Significant at the 1% level

The mean $c_1$ values and the coefficients of variation are shown for each crop in Table 6. The coefficient of variation in $c_1$ values was relatively large although the standard error of estimate, Sy, was reasonably small. About 10 per cent of the plots for each crop gave unusually high percentage yields. In fact the $c_1$ values for some of these plots were more than twice the mean $c_1$ value for all plots and accounted for a large proportion of the variability in $c_1$ values indicated in Table 6. Because these high percentage yield values fall on the relatively flat portion of the logarithmic yield curve, they had a relatively small effect on the standard error of estimate (Sy). The correlation between percentage yield decrement, Log $(100-y)$, and soil test value was highly significant for all crops. None of the plots from which the statistics in Table 6 were calculated had received large additions of organic matter during the previous year. Additional oats plots, however, were located where cornstalks had been ploughed down the previous fall. The $c_1$ values and the Sy values for these plots indicated a wide divergence from the averages reported here. It was evident that some correction is required in the soil test method itself, or in the calculation, before the test result will give a satisfactory correlation with yield of crops following recent addition of organic material. As sufficient data become available, it may be possible to determine a different mean $c_1$ value for these instances.

For soils that had received only root and stubble residues of crops, the modified incubation method did give a reasonably satisfactory correlation with crop yield. Additional field data and further refinements in the modified incubation method may lead to still better correlation.

## REFERENCES

1. Allison, F. E., and L. D. Sterling. Nitrate formation from soil organic matter in relation to total nitrogen and cropping practices. Soil Sci. 67:239–252. 1949.
2. Bray, R. H. Correlation of soil tests with crop response to added fertilizer and with fertilizer requirements. *In* Diagnostic techniques for soils and crops, pp. 58–86. American Potash Institute, Washington, D. C. 1948.
3. Briggs, L. J., and J. W. McLane. The moisture equivalent of soils. U.S.D.A. Bureau of Soils Bull. 45. 1907.
4. Canada Department of Agriculture. Report of Director of Science Service, 1955–1956.
5. Cook, F. D., F. G. Warder, and J. L. Doughty. Relationship of nitrate accumulation to yield response of wheat in some Saskatchewan soils. Can. J. Soil Sci. 37: 84–88. 1957.
6. Fitts, J. W., W. V. Bartholomew, and H. Heidel. Correlation between nitrifiable nitrogen and yield response of corn to nitrogen fertilization on Iowa soils. Soil Sci. Soc. Amer. Proc. 17:119–122. 1953.
7. Hanway, J., and L. Dumenil. Predicting nitrogen fertilizer needs of Iowa soils:III. Use of nitrate production together with other information as a basis for making nitrogen fertilizer recommendations for corn in Iowa. Soil Sci. Soc. Amer. Proc. 19:77–80. 1955.
8. Harmsen, G. W., and D. A. Van Schreven. Mineralization of organic nitrogen in soil. Advances in agronomy, VII, pp. 300–383. 1955.
9. Munson, R. D., and G. Stanford. Predicting nitrogen fertilizer needs of Iowa soils:IV. Evaluation of nitrate production as a criterion of nitrogen availability. Soil Sci. Soc. Amer. Proc. 19: 464–468. 1955.
10. Saunder, D. H., B. L. Ellis, and A. Hall. Estimation of available nitrogen for advisory purposes in Southern Rhodesia. J. Soil Sci. 8:301–312. 1957.
11. Stanford, G., and J. Hanway. Predicting nitrogen fertilizer needs of Iowa soils:II. A simplified technique for determining relative nitrate production in soils. Soil Sci. Soc. Amer. Proc. 19:74–77. 1955.
12. Starkey, R. L. Some influences of the development of higher plants upon the microorganisms in the soil:V. Effects of plants upon distribution of nitrates. Soil Sci. 32:395–404. 1931.

# A MINERALOGICAL AND CHEMICAL STUDY OF THE DIKELAND SOILS OF NOVA SCOTIA[1]

J. E. BRYDON AND H. HEYSTEK[2]

*Canada Department of Agriculture, Ottawa, Ontario*

[Received for publication January 28, 1958]

## ABSTRACT

Six profiles taken from the dikeland areas of Nova Scotia were examined chemically and mineralogically. The mineralogy of the various layers was similar within and between profiles, except that the reddish layers contained goethite while the grey layers did not. The latter were very strongly acidic and had an unusually high organic matter content due to burial of undecomposed vegetation by tidal sediments. While they contained no goethite, they had a significant amount of "free iron". It is proposed that where sufficient organic matter was available the grey layers were produced by anaerobic bacterial reduction of the reddish iron oxides.

Quartz was the predominant non-clay mineral associated with mica, feldspar and chlorite. The clay fraction consisted of illite with characteristics of muscovite, chlorite similar to "swelling" chlorite, kaolinite and montmorillonite.

## INTRODUCTION

Mineralogical and chemical studies have been conducted with a view to characterizing the dikeland soils adjacent to the Bay of Fundy in Nova Scotia and New Brunswick, and to explain the presence of grey layers associated with the predominantly reddish material. These grey layers occur at various depths underlying or sandwiched between reddish layers, or exposed at the surface. There appears to be no evidence of podzolization in the diked sediments. It has been proposed that the greying has some relationship with poor drainage, and an attempt has been made to classify the dikeland soils on the basis of five drainage members which are correlated with depth to the grey layer in the profile (1). This classification is not applicable to all soils and, therefore, other factors possibly operate in addition to poor drainage.

The dikeland soils are marine deposits which have been built up over a long period of time. Extensive areas are inundated by the extremely high tides and, when the water recedes, a deposit of silty material remains. Because of the variation in height of the tides, sedimentation is irregular and undecomposed sedgy organic material may be buried. The sediments are believed to be derived from the soft Carboniferous and Triassic sandstones and shales of the surrounding uplands and underlying the Bay of Fundy (19). At the present time the fresh sediments are reddish and have never been known to be greyish. When properly protected by dikes, the deposits develop into the most productive agricultural soils in the region and large areas have thus been reclaimed.

The present study was initiated to determine the chemical and mineralogical characteristics of the various materials in the major dikeland areas. From this an explanation is proposed for the formation of the grey layers. Because of the complexity of the clay mineral assemblage, the identification and characterization of the clay minerals is emphasized.

---

[1]Contribution No. 389, Chemistry Division, Science Service, Canada Department of Agriculture, Ottawa, Ont.
[2]Post-doctorate Fellow, Chemistry Division, 1955-56. *Present address:* National Chemical Research Laboratory, South African Council for Scientific and Industrial Research, Pretoria, South Africa.

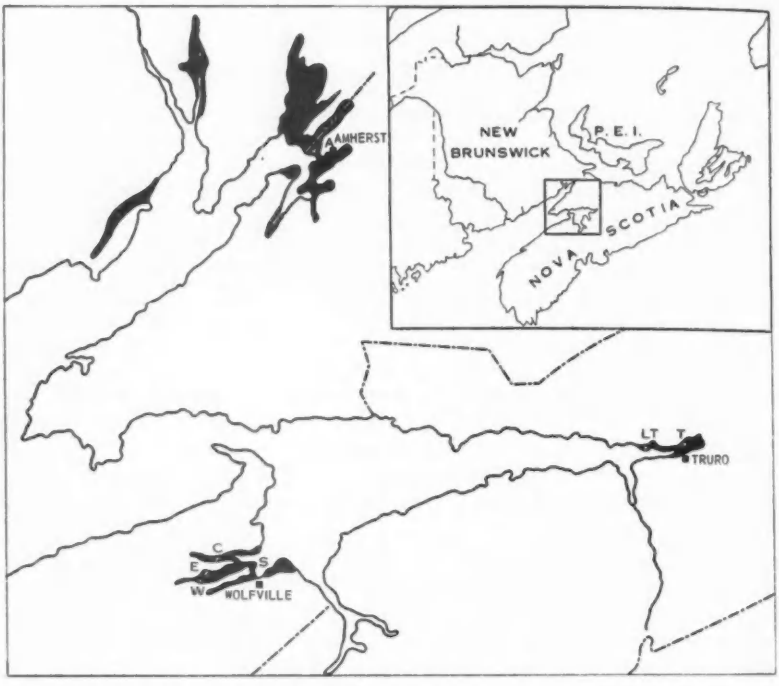



FIGURE 1. Map of the Maritime Provinces, showing the major dikeland areas and the sampling sites.

## SOIL PROFILES

Profiles were taken from three major areas: near Amherst (A); near Truro (T and LT); and north of Wolfville (C, E, and W, Figure 1). Because the dikeland soils showed no evidence of genetic horizon differentiation, the profiles were sampled as layers according to differences in colour, texture and consistency as shown in Table 1. For convenience, the layers have been assigned letters and numbers beginning at the surface so that, for example, $LT_1$ represents the 0–6″ layer of the Lower Truro profile. Following is a description of the profiles sampled.

The Amherst profile was taken from the Amherst Marsh at the head of Cumberland Basin, 2½ miles west of Amherst on the east side of the LaPlanche River. This area has been protected from inundation for perhaps as many as 100 years. It is classified as imperfectly drained.

The Truro profile was taken from the Onslow Marsh at the head of Cobequid Bay, 3 miles west of Truro. The area is fairly well drained and has been diked for many years. The internal drainage appeared to be moderately rapid in the surface 12 inches but slower with depth. Mottling occurs below 24 inches and becomes pronounced with depth.

TABLE 1.—COLOUR AND TEXTURE OF THE PROFILE SAMPLES

| Designation | Depth (in.) | Colour | Munsell reading | Texture |
|---|---|---|---|---|
| **Amherst** | | | | |
| $A_1$ | 0–6 | dk. red br. | 5YR3/3 | si.c.l. |
| $A_2$ | 6–10 | dk. red grey | 5YR4/2 | si.c.l. |
| $A_3$ | 10–16 | grey | 10YR5/1 | si.c.l. |
| $A_4$ | 16–22 | dk. red br. | 5YR3/4 | si.c.l. |
| $A_5$ | 36–40 | dk. red grey | 5YR4/2 | si.l. |
| $A_6$ | 48– | dk. red grey | 5YR4/2 | si.l. |
| **Truro** | | | | |
| $T_1$ | 0–12 | dk. red br. | 5YR3/4 | si.l. |
| $T_2$ | 12–24 | dk. red br. | 5YR3/4 | si.l. |
| $T_3$ | 24–48 | red br. | 5YR4/4 | si.l. |
| $T_4$ | 48–60 | red br. | 5YR4/4 | si.l. |
| $T_5$ | 60–72 | red br. | 5YR4/4 | si.l. |
| **Lower Truro** | | | | |
| $LT_1$ | 0– 6 | dk. red grey | 5YR4/2 | si.l. |
| $LT_2$ | 6–12 | dk. red grey | 5YR4/2 | si.l. |
| $LT_3$ | 12–28 | red br. | 5YR4/3 | si.l. |
| $LT_4$ | 28–36 | dk. grey br. | 10YR4/2 | si.c.l. |
| **Canning** | | | | |
| $C_1$ | 0–15 | dk. red br. | 5YR3/3 | si.c.l. |
| $C_2$ | 15–25 | dk. grey | 10YR4/1 | si.c.l. |
| $C_3$ | 25–36 | v. dk. grey | 10YR3/1 | si.c.l. |
| $C_4$ | 36–60 | dk. grey | 10YR4/1 | si.c.l. |
| **Eaton** | | | | |
| $E_1$ | 0– 7 | dk. red br. | 5YR3/3 | si.c.l. |
| $E_2$ | 7–15 | grey br. | 10YR5/2 | si.c.l. |
| $E_3$ | 15–24 | grey br. | 10YR5/2 | si.c.l. |
| $E_4$ | 32–36 | grey | 10YR5/1 | si.c.l. |
| **Wellington** | | | | |
| $W_1$ | 0– 6 | dk. red br. | 5YR3/2 | si.c.l. |
| $W_2$ | 6–14 | dk. red br. | 5YR3/3 | si.c. |
| $W_3$ | 14–26 | red br. | 5YR4/3 | si.c. |
| $W_4$ | 26–36 | red br. | 5YR4/3 | si.c. |
| $W_5$ | 36–42 | red br. | 5YR4/3 | si.c. |
| $W_6$ | 42–48 | dk. red br. | 5YR3/3 | si.c.l. |
| $W_7$ | 48–60 | dk. red br. | 5YR3/3 | si.l. |
| $W_8$ | 68–74 | dk. red grey | 5YR4/2 | si.l. |
| **Fresh sediment** | | | | |
| S | | red br. | 5YR4/3 | si.c.l. |

The Lower Truro profile was taken from the Masstown Marsh near Debert, about 12 miles west of Truro on the north side of Cobequid Bay. The area has been flooded intermittently since reclamation due to occasional breaks in the dikes, though not during the past 5 or 6 years. Vegetation is largely marsh grass, sedges and salt-tolerant species, and remains of this vegetation in various stages of decomposition are found embedded in the subsoil. The surface layers of both the Truro and Lower Truro have a well developed medium to fine blocky structure and the material becomes massive with depth. The grey layer is prominently mottled with yellowish brown stains.

The Canning profile was taken about a mile east of Canning Village on a new marsh area where the Habitant River empties into Minas Basin. This area was diked in 1945 and is poorly drained. The vegetation consists of salt-tolerant grasses and sedges, remains of which are found in the lower subsoil. When the profile was exposed, the odour of hydrogen sulphide was exceptionally strong.

The Eaton profile was taken on the Canard River dikeland area about 1 mile east of Upper Canard Village. The area is well drained and is alleged to have been free from flooding for about 200 years. The subsoil has prominent yellow and brown mottling and, below 36 inches, a dark organic layer of well-preserved plant residue.

The Wellington profile was taken from the Canard River dikeland area about a mile south of the Eaton profile site and 50 yards from the Canard River. It has been free from flooding for about the same time as the Eaton profile. Faint mottling occurred at about 36 inches.

The fresh sediment sample S was taken from a recently deposited sediment in the Canard River.

TABLE 2.—MECHANICAL COMPOSITION (AS PER CENT OF TOTAL MINERAL MATTER)

| | >50 micron | 50–20 micron | 20–5 micron | 5–2 micron | 2–0.2 micron | <0.2 micron |
|---|---|---|---|---|---|---|
| $A_1$ | 4.4 | 26.1 | 33.3 | 6.9 | 21.9 | 7.5 |
| $A_2$ | 2.3 | 26.4 | 33.1 | 7.5 | 21.7 | 8.9 |
| *$A_3$ | 1.4 | 15.5 | 35.5 | 9.8 | 25.8 | 12.0 |
| $A_4$ | 3.6 | 22.0 | 32.8 | 8.8 | 28.1 | 4.7 |
| $A_5$ | 12.0 | 44.0 | 22.2 | 7.2 | 14.7 | — |
| $A_6$ | 11.6 | 53.5 | 20.3 | 4.6 | 10.0 | — |
| $T_1$ | 11.0 | 54.6 | 15.9 | 5.5 | 9.6 | 3.4 |
| $T_2$ | 10.0 | 46.7 | 18.5 | 7.0 | 10.5 | 6.8 |
| $T_3$ | 6.1 | 48.9 | 19.5 | 7.0 | 11.3 | 7.2 |
| $T_4$ | 22.2 | 53.7 | 10.8 | 4.0 | 6.4 | 2.9 |
| $T_5$ | 31.1 | 52.4 | 7.0 | 2.4 | 5.2 | 2.0 |
| $LT_1$ | 4.6 | 39.1 | 23.1 | 8.8 | 14.5 | 9.9 |
| $LT_2$ | 4.9 | 41.5 | 22.0 | 7.9 | 13.5 | 10.1 |
| $LT_3$ | 3.4 | 44.9 | 20.8 | 7.7 | 14.1 | 9.1 |
| *$LT_4$ | 2.2 | 18.6 | 27.7 | 13.5 | 22.5 | 15.5 |
| $C_1$ | 3.1 | 22.3 | 28.6 | 12.6 | 20.0 | 13.4 |
| *$C_2$ | 2.4 | 14.5 | 28.4 | 15.5 | 24.8 | 14.5 |
| *$C_3$ | 5.1 | 18.0 | 27.0 | 14.8 | 29.8 | 5.3 |
| *$C_4$ | 4.6 | 17.5 | 30.1 | 15.7 | 23.7 | 8.4 |
| $E_1$ | 4.7 | 18.5 | 36.0 | 7.0 | 20.8 | 13.1 |
| $E_2$ | 6.4 | 16.0 | 38.9 | 8.1 | 21.0 | 9.7 |
| $E_3$ | 9.4 | 10.9 | 40.4 | 5.8 | 22.4 | 11.1 |
| *$E_4$ | 4.9 | 13.8 | 40.7 | 4.4 | 23.3 | 12.9 |
| $W_1$ | 0.7 | 10.1 | 36.8 | 18.9 | 21.8 | 11.7 |
| $W_2$ | 1.0 | 7.2 | 32.8 | 13.8 | 28.8 | 16.5 |
| $W_3$ | 1.0 | 4.9 | 35.3 | 13.8 | 28.7 | 16.3 |
| $W_4$ | 0.5 | 5.9 | 30.7 | 14.2 | 31.7 | 17.0 |
| $W_5$ | 2.7 | 6.7 | 33.1 | 15.2 | 28.2 | 14.0 |
| $W_6$ | 9.2 | 15.0 | 29.4 | 12.2 | 22.7 | 11.5 |
| $W_7$ | 15.2 | 32.7 | 22.9 | 8.8 | 15.4 | 5.0 |
| $W_8$ | 24.0 | 42.3 | 14.0 | 6.2 | 9.9 | 3.6 |
| S | 1.9 | 12.1 | 36.2 | 15.1 | 23.5 | 11.2 |

*Grey layers.

## METHODS

### *Mechanical Analysis*

The soils were fractionated after $H_2O_2$ treatment into >50, 50–20, 20–5, 5–2 and <2 micron separates by normal sedimentation techniques. The <0.2 micron clay fraction was separated from the <2 micron clay suspension by centrifugation. It was then concentrated by flocculation with acidified $CaCl_2$, washed free of chloride with ethyl alcohol, dried and weighed. The sediment remaining from the latter separation was the 2–0.2 micron fraction.

### *Mineralogical Analysis*

*Non-clay Fractions*—X-ray diffraction patterns of non-oriented specimens of the silt and sand fractions were obtained with a Philips X-ray diffractometer using Fe-filtered Co radiation throughout. In addition, some of the samples were examined using 114.6 mm. Debye-Sherrer X-ray powder cameras in order to obtain enhanced (hkl) reflections.

*Clay Fractions*—Non-oriented specimens of the clay fractions were investigated, using the X-ray diffractometer in a manner identical with that used for the silts and sands.

Oriented specimens were prepared by triturating suspensions of the clays in water, applying them to glass microscope slides and allowing them to dry. The resulting thin film specimens were X-rayed following solvation with ethylene glycol or heating, as will be explained later.

*Chemical Analyses*

The exchangeable cations, cation exchange capacity, pH and organic matter were determined using the usual techniques of this laboratory (8). Total $Fe_2O_3$ and ferrous iron were determined by the methods of Shapiro and Brannock (15). McKenzie's method (12) was used to remove and determine free iron oxides. Total potassium was determined by the method of Corey and Jackson (9).

## RESULTS

*Mechanical Analysis*

There was some variation in texture within and between profiles (Table 2), but in all cases the silt fraction predominated. All of the grey layers were fine-textured, but were not unique in this respect since the top six reddish Wellington layers were the finest textured. The differences in textural composition in the samples may be attributed to variations in velocity of the tidal waters at the time of deposition.

*Mineralogy*

*The Non-clay Fractions*—All silt and sand fractions contained significant amounts of quartz, feldspar, mica and chlorite. From X-ray diffraction data, it was found that fractions having the same size limits had the same proportions of these minerals, irrespective of the profile or layer from which they were separated. However, in any one layer there was a significant difference in the diffraction patterns between different size fractions.

This difference involved chiefly the quartz and feldspar reflections (Figure 2). As the particle size decreased, the quartz peak at 4.25A and the feldspar peak at 3.20A decreased in intensity. The chlorite peaks at 14, 7.2, 4.75 and 3.6A varied slightly but had approximately the same intensity in all silt and sand fractions. The mica basal reflections at 10 and 5A followed the same pattern, but the (020) mica reflection at 4.48A increased markedly with decrease in particle size. The different diffraction effects of the feldspar, mica and chlorite species and the variation in degree of alteration of these species with particle size, superimposed upon the various potential diffraction errors cited by Brindley (5), made a quantitative estimation of these minerals hazardous. The diffraction pattern of quartz is the least affected by these factors so it is reasonable to state that the amount of quartz decreased gradually with particle size. Mica is the most likely mineral increasing in amount to account for the remainder.

Examination of the sand fraction, using the petrographic microscope, revealed that there was roughly 40 per cent quartz, 10 per cent muscovite, 10 per cent biotite, 10 per cent chlorite and 20 per cent feldspar, with the

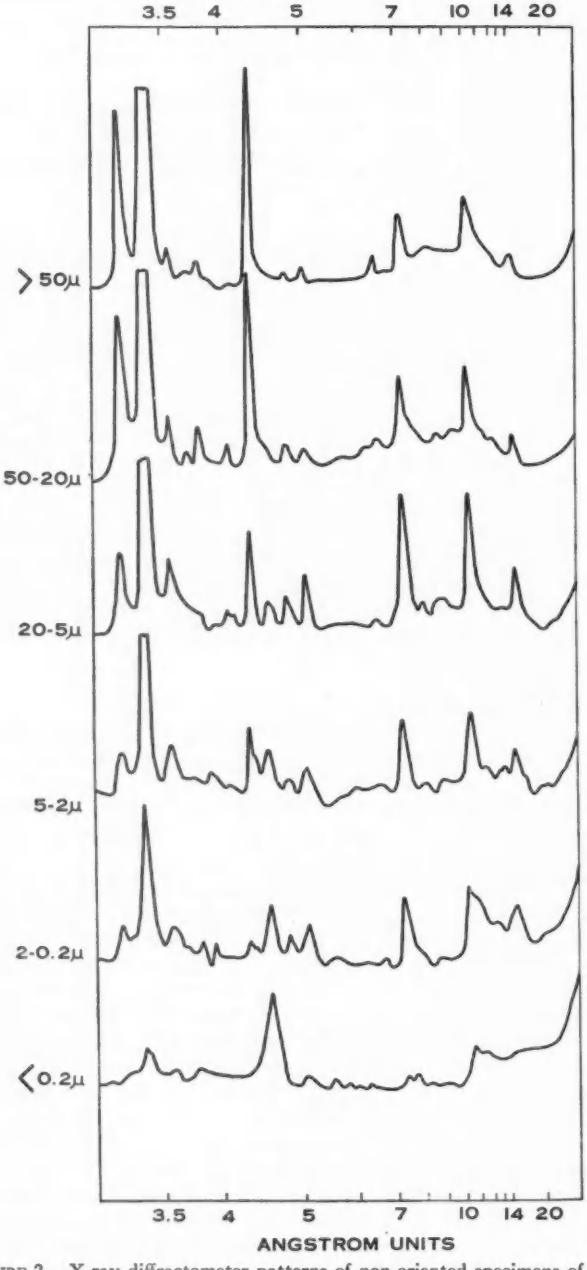



FIGURE 2. X-ray diffractometer patterns of non-oriented specimens of designated size fractions from sample $W_4$.

remaining 10 per cent consisting of amphiboles, pyroxenes, opaque minerals, tourmaline and others. The feldspars were altered considerably but the majority appeared to be plagioclase.

*The Clay Fractions*—X-ray diffraction procedures indicated that the clay fractions from different samples were mineralogically similar but, as in the non-clay fractions, the mineralogy of the two fractions from the same layer differed.

Patterns of an oriented specimen of the <0.2 micron fraction (Figure 3) revealed the presence of illite and montmorillonite with weak chlorite and kaolinite reflections. Upon solvation, two peaks at 10 and 17A were observed which merged into a 10A component upon mild heat treatment, a characteristic feature of a mixture of montmorillonite and illite. During these and higher heat treatments, the orders of illite basal spacings at 10, 5, 3.33, and 2A persisted. Up to a temperature of 400°C. there were distinct peaks at 7.2 and 3.6A, indicating kaolinite, chlorite, or both, and a 4.75A shoulder on the high angle side of the 5A illite peak showing the presence of chlorite. These features disappeared and a very weak 14.5A reflection appeared on heating to 500°C., both of which are characteristic of chlorite in the presence or absence of kaolinite (11). The medium peak at 7.2 and the weak 14.5 and 4.75A chlorite peaks suggested that kaolinite contributed to the 7.2A feature in addition to chlorite.

X-ray diffraction patterns (Figure 4) of an oriented specimen of one of the 2–0.2 micron fractions showed that this fraction consisted of a mixture of several clay minerals. The presence of illite was established by a sequence of strong basal reflections at 10, 5, 3.33, 2.5, and 2.0A, which persisted after solvation, after heating to 700°C. and after hot 0.1 N HCl treatments. Montmorillonite was detected, after solvation, by a weak reflection in the 17A region which, upon heating to 200° C., disappeared and apparently collapsed to give an enhanced 10A reflection. Chlorite was shown by the effect of heating at 500° C. on the basal spacings; the 14.5A peak became more intense and the 7.2, 4.75, 3.6, and 2.84A disappeared at this temperature. However, although the intensity of the 14.5A reflection of well-crystallized chlorites remains unchanged up to this temperature (5) this reflection from the present specimen was more intense at 200° C. than at 300 or 400° C. There is the possibility that vermiculite contributed to the 14.5A feature at low temperatures and, by collapse to 10A, accounted for the decrease in intensity at 300° C. (13).

In some of the coarse clay specimens, there was a doublet in the 3.6A region and a very weak peak at 2.39 which, according to Bradley (4), are characteristic of kaolinite reflections superimposed upon those of chlorite. In order to establish the presence of kaolinite, one of the 2–0.2 micron fractions was subjected to hot 0.1 N HCl treatments (5). Samples were examined periodically and after one hour the 14.5 and 4.75A reflections, which are characteristic of chlorite, disappeared. Since 7.2 and 3.6A reflections persisted, kaolinite must have been present and was not destroyed during the acid treatment.

The data obtained from the heating and acid treatments of the coarse clay offer a clue as to the nature of the chlorite component. Acid treatment

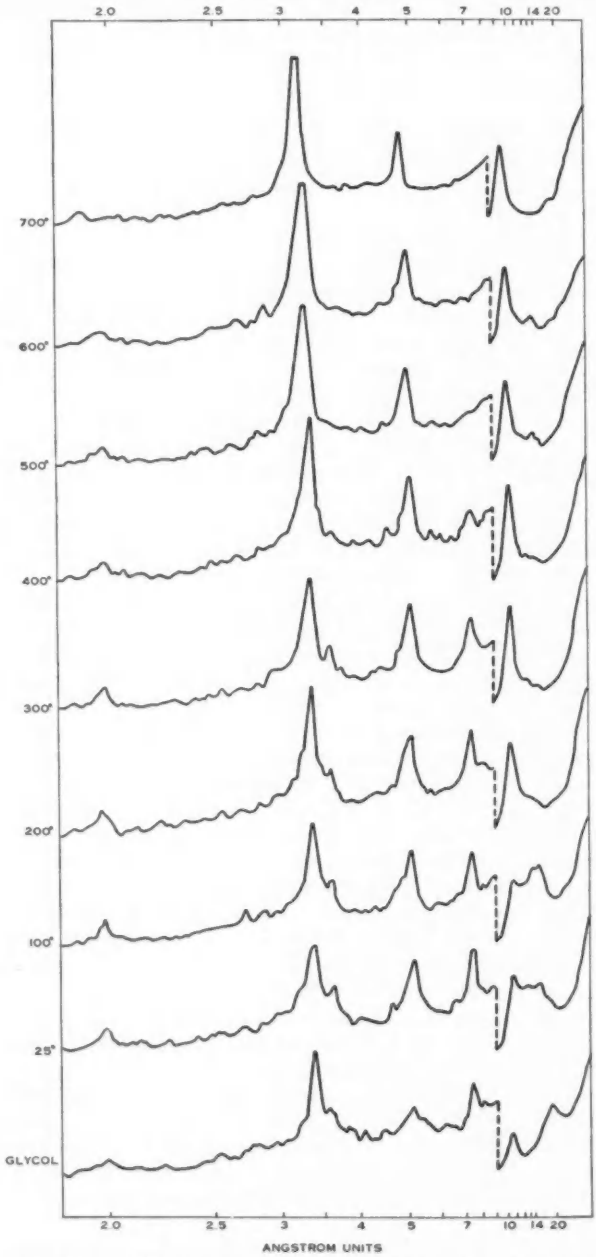



FIGURE 3. X-ray diffractometer patterns of an oriented specimen of the <0.2 micron fraction from sample $W_4$, after designated treatments. The counting rate was doubled below 8A (broken line).

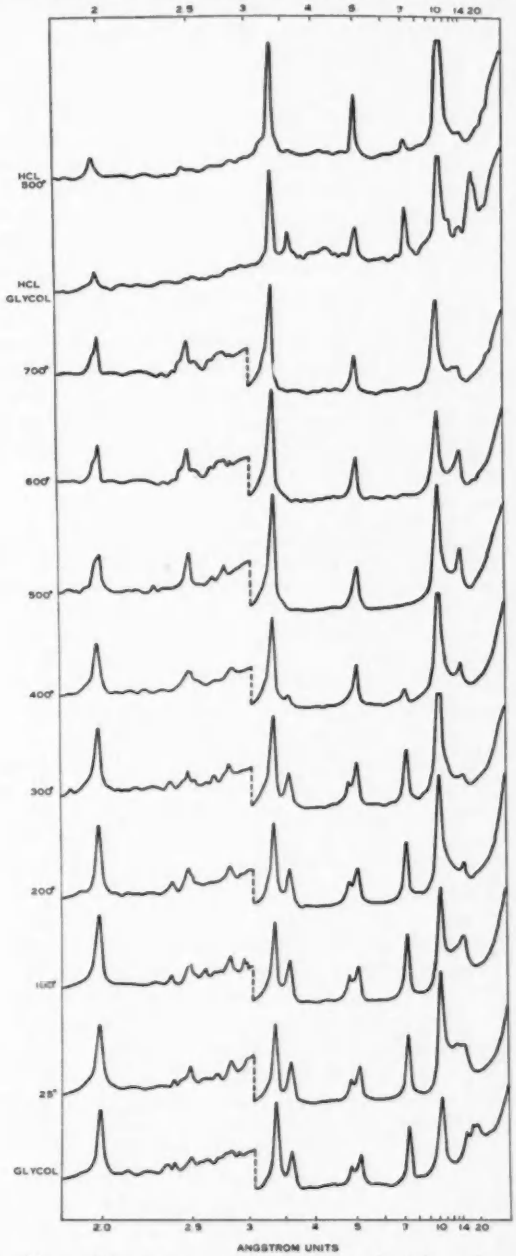



FIGURE 4. X-ray diffractometer patterns of an oriented specimen of the 2–0.2 micron fraction from sample $W_4$, after designated treatments.

of well-crystallized chlorite has been shown to remove the octahedral layer of the talc-like portion as well as the brucitic interlayer material (6), whereas with "swelling" chlorites, the brucitic layer may be removed without decomposition of the talc-like portion of the lattice (7). In the present case, since the acid treatment produced an enhanced montmorillonite 17A reflection upon solvation, the talc-like portion was not destroyed and the chlorite behaved like "swelling" chlorite. Taking into account the temperature at which the basal spacings altered in intensity, it was inferred that the chlorite was not as stable as well-crystallized chlorites (11), that it had a higher stability than the authigenic chlorite from the Gulf of Mexico (11) and that its heat stability was similar to the "swelling" chlorite cited by Stephen and MacEwen (17). Thus, from both the acid and heat treatments, it is concluded that the chlorite component has a degree of crystal disorder similar to that of "swelling" chlorite, although the presence of swelling layers in the chlorite could not be distinguished from montmorillonite. The above results serve to demonstrate the lack of knowledge of clay-size chlorites; one is unable to link departures from the properties of well-crystallized chlorites to a specific type.

TABLE 3.—X-RAY DIFFRACTION DATA OF THE 2–0.2 AND <0.2 MICRON CLAY FRACTIONS OF $W_4$

| 2–0.2 micron | | <0.2 micron | | 2–0.2 (cont'd) | | <0.2 (cont'd) | |
|---|---|---|---|---|---|---|---|
| I | d | I | d | I | d | I | d |
| 4 | 14.25 | 5 | 15.31 | ½ | 2.203 | 1 | 2.202 |
| | | | 13.86 | 1½ | 2.128* | ½ | 2.131 |
| 3 | 10.02 | 3½ | 10.47 | vb | 2.063 | | — |
| | | | 9.926 | 1 | 2.000 | ½b | 1.994 |
| 2 | 7.137 | 1½ | 7.137 | ½ | 1.974* | | — |
| v | 5.625 | | — | v | 1.889 | | — |
| ½ | 4.979 | 1 | 4.979 | v | 1.842 | ½ | 1.841 |
| v | 4.752 | | — | 1½ | 1.816* | | — |
| 6 | 4.467 | 10 | 4.467 | v | 1.738 | | — |
| 2 | 4.260* | | — | ½ | 1.694 | 1½ | 1.696 |
| v | 4.126 | v | 4.142 | ½ | 1.671* | | — |
| v | 4.031 | | — | ½ | 1.648 | vb | 1.644 |
| 1 | 3.888 | v | 3.874 | v | 1.624 | | — |
| 1b | 3.718 | 1½ | 3.692 | ½ | 1.600 | v | 1.598 |
| 1½b | 3.509 | 1 | 3.520 | 1½ | 1.540* | v | 1.537 |
| 10 | 3.343* | 3 | 3.337 | 3½ | 1.498 | 3 | 1.498 |
| 2½ | 3.193 | 1 | 3.193 | v | 1.488 | ½ | 1.483 |
| 1½ | 2.991 | ½ | 2.983 | ½ | 1.451* | 1 | 1.451 |
| ½ | 2.856 | v | 2.861 | v | 1.414* | | — |
| ½ | 2.787 | v | 2.801 | ½ | 1.380 | v | 1.372 |
| ½ | 2.700 | 1½ | 2.693 | 1 | 1.372* | | — |
| 3 | 2.588 | 3½ | 2.588 | v | 1.353 | v | 1.351 |
| 5 | 2.554 | 4½ | 2.560 | v | 1.338* | | — |
| v | 2.517 | 2 | 2.511 | 1b | 1.298 | 1½ | 1.296 |
| 2 | 2.455* | ½ | 2.441 | | 1.288* | | — |
| 2 | 2.386 | 1½ | 2.381 | v | 1.266 | | — |
| v | 2.337 | | — | ½ | 1.254* | | — |
| ½ | 2.280* | | — | v | 1.247 | ½ | 1.246 |
| ½b | 2.243 | 1 | 2.250 | v | 1.218* | | — |

*Quartz.

TABLE 4.—POTASSIUM IN THE CLAY FRACTIONS OF SOME REPRESENTATIVE SAMPLES
(Expressed as per cent of $K_2O$)

| Sample | 2–0.2 micron | <0.2 micron |
|---|---|---|
| $A_2$ | 3.83 | 3.81 |
| $A_3$ | 4.07 | — |
| $T_3$ | 4.05 | 3.88 |
| $LT_3$ | 3.77 | — |
| $C_1$ | 3.97 | — |
| $C_3$ | 3.64 | — |
| $E_2$ | 4.03 | — |
| $W_4$ | 3.81 | 3.48 |
| S | 3.70 | — |

An attempt was made to characterize further the mineralogy of both clay fractions by means of powder camera data (Table 3). The majority of d-spacings of the coarse clay fraction corresponded to a mixture of illite and quartz. From the illite reflections, it was found that the (060) feature at 1.50A showed it to be dioctahedral. Furthermore, using Smith and Yoder's notations (16), the illite d-spacings corresponded to a mixture of 1M and 2M muscovites. The illite d-spacings from the fine fractions also had these muscovite characteristics even though the reflections were not as sharp as in the coarse. Quartz reflections were absent from the pattern of the fine clay. Feldspar could not be positively identified because its characteristic reflections coincide with those of the mica. However, a comparison of the intensities of the 3.72A and 3.19A lines (feldspar and muscovite) with those of the other muscovite spacings indicated that feldspar was probably present. Goethite was identified by only two peaks (4.13A and 2.70A) which were present in both the fine and coarse fractions of the reddish but not the grey samples. There were chlorite and kaolinite reflections in both fractions, including a weak chlorite (060) feature at 1.54A. This could be attributed to trioctahedral micas but none of the other d-spacings could be used to establish its presence along with the dioctahedral type.

Several of the clays were analysed for total potassium in order to calculate the amount of illite, assuming that essentially all the potassium was in the illite. The values (Table 4) corresponded to the lower limits of $K_2O$ cited by Grim (10) for a series of illites, which Smith and Yoder (16) have shown to consist of polymorphic forms of muscovite with various proportions of hydrated layers. If the latter concept is adopted, then the lowest value of $K_2O$ corresponded to 29.5 per cent illite and the highest to 34.5 per cent illite, using 11.8 per cent $K_2O$ in muscovite as reference. These percentages are consistent with the X-ray data. The equal amounts of $K_2O$ in the fine and coarse fractions led to the conclusion that there was an equal amount of illite in each.

Differential thermal analysis supported the other evidence on clay mineralogy. Two low temperature peaks at 120° and 180° C. corresponded to the loss of absorbed water from Ca-montmorillonite. The endothermic peak at 570° C. corresponded to the temperature at which illites lose lattice hydroxyl under these experimental conditions.

TABLE 5.—IRON CONTENT OF AIR-DRY SOILS
(as per cent $Fe_2O_3$)

| | Total | Free | Silicate |
|---|---|---|---|
| $A_1$ | 6.00 | 2.58 | 3.42 |
| $A_2$ | 5.88 | 2.02 | 3.86 |
| *$A_3$ | 4.92 | 1.06 | 3.86 |
| $A_4$ | 6.96 | 2.78 | 4.18 |
| $A_5$ | 5.04 | 1.80 | 3.24 |
| $A_6$ | 5.20 | 1.72 | 3.58 |
| $T_1$ | 3.40 | 1.20 | 2.20 |
| $T_2$ | 4.20 | 1.58 | 2.62 |
| $T_3$ | 3.80 | 1.40 | 2.40 |
| $T_4$ | 2.70 | 0.94 | 1.76 |
| $T_5$ | 2.60 | 0.68 | 1.92 |
| $LT_1$ | 4.84 | 1.68 | 3.16 |
| $LT_2$ | 4.80 | 1.96 | 2.84 |
| $LT_3$ | 5.08 | 2.16 | 2.92 |
| *$LT_4$ | 4.12 | 0.92 | 3.20 |
| $C_1$ | 5.88 | 2.52 | 3.36 |
| *$C_2$ | 4.72 | 1.36 | 3.36 |
| *$C_3$ | 5.88 | 2.16 | 3.72 |
| *$C_4$ | 5.45 | 0.66 | 4.79 |
| $E_1$ | 5.32 | 2.62 | 2.70 |
| $E_2$ | 5.40 | 2.20 | 3.20 |
| $E_3$ | 5.40 | 2.74 | 2.66 |
| *$E_4$ | 4.84 | 1.68 | 3.12 |
| $W_1$ | 6.28 | 2.46 | 3.82 |
| $W_2$ | 6.96 | 2.66 | 4.30 |
| $W_3$ | 7.20 | 2.64 | 4.56 |
| $W_4$ | 6.96 | 2.68 | 3.72 |
| $W_5$ | 7.32 | 2.66 | 4.66 |
| $W_6$ | 6.04 | 2.26 | 3.78 |
| $W_7$ | 5.44 | 2.14 | 3.30 |
| $W_8$ | 4.56 | 1.54 | 3.02 |
| S | 6.40 | 1.61 | 4.79 |

*Grey layers.

Combining the data obtained by X-ray diffraction, chemical analysis and differential thermal analysis, the following conclusions may be made: The 2–0.2 micron clay fractions consisted mainly of illite which had characteristics of muscovites and, in addition, quartz, montmorillonite, kaolinite and a chloritic component which had some characteristics similar to "swelling" chlorite. Feldspar was probably also present in this fraction. The fine clays had a significant amount of illite with muscovite characteristics. There appeared to be a higher proportion of montmorillonite in the fine than in the coarse clay fraction. Chlorite and kaolinite were present but quartz and feldspar were absent in the fine fraction. Both fractions of reddish samples contained goethite but none was present in the grey layers.

TABLE 6.—CHEMICAL CHARACTERISTICS OF PROFILE SAMPLES

| | pH[1] | % Saturation | | | | C.E.C.[2] | Organic matter[3] |
|---|---|---|---|---|---|---|---|
| | | K | Ca | Mg | H | me./100 gm. | % |
| $A_1$ | 4.20 | 1.6 | 11.4 | 16.4 | 70.5 | 20.2 | 6.32 |
| $A_2$ | 4.35 | 2.5 | 15.8 | 25.7 | 55.9 | 19.8 | 2.62 |
| *$A_3$ | 4.20 | 2.2 | 8.2 | 16.3 | 73.2 | 19.1 | 3.19 |
| $A_4$ | 4.10 | 2.2 | 8.5 | 19.0 | 70.3 | 18.6 | 2.26 |
| $A_5$ | 3.95 | 2.7 | 9.2 | 13.1 | 75.1 | 11.7 | 1.88 |
| $A_6$ | 3.20 | 0.8 | 14.6 | 28.0 | 56.6 | 14.9 | 1.54 |
| $T_1$ | 5.25 | 1.1 | 30.3 | 32.4 | 36.2 | 9.7 | 1.43 |
| $T_2$ | 6.80 | 2.9 | 25.6 | 39.6 | 32.0 | 10.9 | .51 |
| $T_3$ | 6.85 | 5.7 | 24.2 | 48.5 | 21.6 | 9.4 | .33 |
| $T_4$ | 6.45 | 4.2 | 17.3 | 48.4 | 30.1 | 10.0 | 1.99 |
| $T_5$ | 5.90 | 4.7 | 23.0 | 45.5 | 26.8 | 5.4 | .32 |
| $LT_1$ | 4.35 | 1.1 | 16.0 | 24.7 | 58.2 | 16.0 | 6.03 |
| $LT_2$ | 4.30 | 1.4 | 22.1 | 34.1 | 42.4 | 13.2 | 3.04 |
| $LT_3$ | 3.75 | 1.6 | 16.8 | 29.3 | 52.4 | 11.5 | 1.26 |
| *$LT_4$ | 3.50 | 2.0 | 12.1 | 21.1 | 64.8 | 22.0 | 8.52 |
| $C_1$ | 3.85 | 3.6 | 10.2 | 23.2 | 63.1 | 17.4 | 2.60 |
| *$C_2$ | 3.50 | 3.4 | 13.0 | 34.6 | 49.0 | 24.0 | 7.94 |
| *$C_3$ | 3.05 | 2.2 | 11.3 | 37.4 | 49.1 | 22.3 | 8.99 |
| *$C_4$ | 5.75 | 10.0 | 22.2 | 53.2 | 14.5 | 19.2 | 6.70 |
| $E_1$ | 4.55 | 1.1 | 52.0 | 13.2 | 33.8 | 21.9 | 4.20 |
| $E_2$ | 3.25 | 1.5 | 8.1 | 17.9 | 72.5 | 17.7 | 1.45 |
| $E_3$ | 3.55 | 1.4 | 5.7 | 14.5 | 78.4 | 18.9 | 1.73 |
| *$E_4$ | 3.35 | 1.6 | 7.6 | 8.3 | 82.5 | 19.0 | 2.67 |
| $W_1$ | 6.45 | 1.5 | 47.0 | 38.0 | 13.4 | 28.2 | 6.67 |
| $W_2$ | 6.90 | 3.9 | 46.7 | 49.4 | — | 21.8 | 1.01 |
| $W_3$ | 7.10 | 5.9 | 43.1 | 50.9 | — | 21.6 | .86 |
| $W_4$ | 7.50 | 5.2 | 46.4 | 48.4 | — | 23.4 | .66 |
| $W_5$ | 7.95 | 7.6 | 50.2 | 42.2 | — | 19.8 | 1.03 |
| $W_6$ | 7.80 | 9.0 | 49.6 | 41.4 | — | 15.6 | 1.22 |
| $W_7$ | 7.95 | 10.6 | 52.4 | 37.0 | — | 12.2 | .95 |
| $W_8$ | 7.15 | 9.1 | 59.3 | 31.6 | — | 9.8 | 1.03 |
| S | 7.70 | 11.3 | 39.5 | 49.2 | — | 19.2 | — |

*Grey layers.
[1]Soil:water ratio 1:1.
[2]Cation exchange capacity by exchange of $NH_4^+$ with NaCl.
[3]Dichromate method.

*Chemical Data*

*Total and Free Iron*—The analyses of total iron and that portion of it which is removed by sodium dithionate (the free iron oxides) (12) are shown in Table 5. McKenzie (12) found little apparent damage to the silicate minerals and a satisfactory removal of the coloured oxides by the treatment. It is assumed, therefore, that the difference between the total and free iron may be assigned to iron in the silicate minerals (Table 5, Column 3).

The amount of free iron in the reddish-coloured samples was highest in the fine-textured materials, presumably because the iron oxides were associated with the large surface area per unit mass of material in the finer-sized fractions. The grey layers differed and had, in general, 1 per cent less free iron than the reddish layers of equivalent texture.

The similarity in the mineralogy of the grey and red layers and the difference in amounts of free iron in them suggest that iron has been mobilized and removed from the grey layers. Bloomfield (3) found a similar distribution of iron oxides in glei horizons and also showed that mottled grey horizons contained more free iron than unmottled ones. From Table 6, it may be seen that the free iron oxide values of the unmottled grey dikeland layers $A_3$, $C_3$ and $C_4$ varied considerably and were not different from the mottled grey layers.

Analysis of some of the samples revealed that the grey layers did not contain more FeO than the reddish layers. Thus the nature of the iron removed from the grey layers by McKenzie's method is unknown. Goethite was identified in the clay fractions of the red layers and may account for the free iron content and colour of them. The free iron of the grey layers must have been in some form which does not form coloured iron oxides readily, since grey dikeland soils have been observed to remain grey upon exposure to air, a feature of glei horizons (14), and since upon heating the clays from the grey layers, the colour changed from grey (5 YR 6/0) to light brown (7.5 YR 6/4) only at 400° to 500° C. These results suggest that the grey layers have similarities to glei horizons.

*Exchange Chemistry and Organic Matter*—The results (Table 6) indicate that generally the fresh sediment and the Wellington profile were neutral to alkaline, had a rather high K per cent saturation, and a Ca saturation similar to that of Mg. The other profiles were acidic, had a lower K per cent saturation, and the Mg content was greater than that of Ca with the exception of the Eaton surface sample.

If the fresh sediment can be used as a guide, the majority of the exchangeable cations at the time of deposition consisted of slightly more Mg than Ca. As the materials became acidic, the basic cations decreased in amount as expected but the Mg persisted at an unusually high level, even after a high acidity had been developed.

The Eaton, Wellington and Canning profiles show the variations in reaction which can occur. The Eaton profile has a low pH throughout as compared to the neutral reaction of the Wellington even though both are alleged to have been free from flooding for 200 years. The poorly-drained Canning profile has developed a low pH after being diked for less than 10 years. In the well-drained Truro profile, the pH is higher than that of the more imperfectly-drained profiles and the acidity may be considered to be caused by leaching the basic cations from the profile. This mechanism cannot be the dominant process in the other acid profiles since the lowest pH is deep in the profile and since the fine-texture would preclude intensive leaching.

There appeared to be some relationship between the presence of organic matter, low pH and incidence of greying in the subsoils. The amount of organic matter in the surface layers was of the same order as would be expected with normal vegetation. All of the grey layers had an unusually high organic matter content arising through burial of undecomposed vegetation. Because of the known imperfect drainage and high water table, anaerobic conditions would prevail. Wherever there is suffi-

cient organic matter, anaerobic bacterial activity would produce a low pH and a loss of iron oxide colour in the same manner as in Bloomfield's laboratory experiments (2). Thus, anaerobic bacterial activity is suggested as a cause of greying.

An examination of the properties of the grey layers in the profiles reveals that they all fit this mechanism. In the Amherst profile, the grey layer $A_2$ has a higher organic matter content than the other subsoil layers even though it has a slightly higher pH than those below it. The Truro, with no grey layers, has a low organic matter content in the subsoil and a high though acidic pH throughout. In the Lower Truro and Eaton profiles, the pH is low and the organic matter high in the grey layers $LT_4$ and $E_4$. A similar condition exists in samples $C_2$, $C_3$ and $C_4$. The Wellington profile presumably did not have sufficient organic matter for marked bacterial action. Thus, all of these soils have the characteristics which would prevail if the proposed mechanism were operating.

Variations in flooding, water table level, rate of sedimentation and burial of organic material in the various dikeland areas may all be factors in determining the characteristics of these soils. The mechanism proposed for the formation of the grey layers appears to be similar to the gleiing process but the pH of these layers is lower than is usually found in glei horizons (2, 3). Because of the low pH, reduction of iron oxides by bacterial activity rather than chemical reduction by degradation products of plant debris (2), appears to be a more plausible mechanism in the formation of the dikeland grey layers. Bloomfield (2) has presented evidence of both ferric and ferrous organic complexes in his experiments on gleiing by fermentation. It may be suggested that these materials could account for the free iron in the acidic grey horizons of the dikeland soils.

## ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of J. R. Wright and D. B. Cann, who collected the samples in 1953, supplied descriptions of the material and suggested this project. The assistance of L. M. Patry and N. M. Miles in the mineralogical analyses, of the Soil Fertility Section for chemical analyses, and of P. C. Stobbe of the Experimental Farms Service and others for their many valuable suggestions, is gratefully acknowledged.

## REFERENCES

1. Aaland, H., and R. E. Wicklund. Soil survey report of southeastern New Brunswick. New Brunswick Soil Survey Rept. 3. 1950.
2. Bloomfield, C. Experiments on the mechanism of gley formation. J. Soil Sci. 2: 196–211. 1951.
3. Bloomfield, C. The distribution of iron and aluminium oxides in gley soils. J. Soil Sci. 3: 167–171.
4. Bradley, W. F. X-ray diffraction criteria for characterization of chloritic material in sediments. "Clays and clay minerals", Publ. 327, U. S. Natl. Research Council, Washington, D. C. 1954.
5. Brindley, G. W. X-ray identification and crystal structures of clay minerals. Mineralogical Soc. Great Britain, London. 1951.
6. Brindley, G. W., and R. F. Youell. A chemical determination of tetrahedral and octahedral aluminum ions in a silicate. Acta Cryst. 4: 495–496. 1951.

7. Caillère, S., S. Hénin, et J. Esquevin. Transformation expérimentale de chlorite en montmorillonite. Clay Minerals Bull. 2: 166–170. 1954.
8. Chemical methods of soil analysis. Chem. Div., Science Service, Can. Dept. Agr., Ottawa. 1949.
9. Corey, R. B., and M. L. Jackson. Silicate analysis by a rapid semi-micro system. Anal. Chem. 25: 624–628. 1953.
10. Grim, R. E. Clay mineralogy. McGraw-Hill Book Co., New York, N. Y. 1953.
11. Grim, R. E., and W. D. Johns. Clay mineral investigation of sediments in northern Gulf of Mexico. "Clays and clay minerals", Publ. 327, U. S. Natl. Research Council, Washington, D. C. 1954.
12. McKenzie, R. C. Free iron-oxide removal from soils. J. Soil Sci. 5: 167–172. 1954.
13. Mitchell, W. A. Discussion period. Clay Minerals Bull. 2: 94. 1953.
14. Russell, E. W. Soil conditions and plant growth. Longmans, Green & Co., London. 1950.
15. Shapiro, L., and W. W. Brannock. Rapid analysis of silicate rocks. U. S. Geol. Survey Bull. 1036C. 1956.
16. Smith, J. V., and H. S. Yoder. Experimental and theoretical studies of the mica polymorphs. Mineral. Mag. 31: 209–235. 1956.
17. Stephen, I., and D. M. C. MacEwen. Some unusual clay minerals of unusual type. Clay Minerals Bull. 1: 157–162. 1951.
18. Whiteside, G. B., R. E. Wicklund, and G. R. Smith. Soil survey of Cumberland County, Nova Scotia. Nova Scotia Soil Survey Rept. 2. 1945.

# NOTE ON RAPID METHOD FOR DETERMINATION OF CARBONATES IN SOILS[1]

To determine the native carbonate content of soil samples from soil survey and other field studies, a manometric method (1, 2) was modified by connecting the reaction vessel to the manometer before mixing the soil and HCl. Continued shaking until no change in pressure occurred was found to be advantageous, since the time required for complete solution of carbonates varies with different soils.

A 1¼-ounce wax paper cup, containing 5 grams of soil, is floated on 30 ml. 4 N HCl in a 700 ml. wide-mouth reaction bottle. A two-hole rubber stopper, carrying thermometer and glass tube, is inserted, the bottle is clamped on a Burrell wrist-action shaker, and a mercury manometer is connected. The shaker will carry eight units. After checking the zero reading on the manometer, the shaker is set in motion, and readings are recorded until no change in pressure occurs.

[1] Contribution No. 400, Chemistry Division, Science Service, Canada Department of Agriculture, Ottawa, Ont.

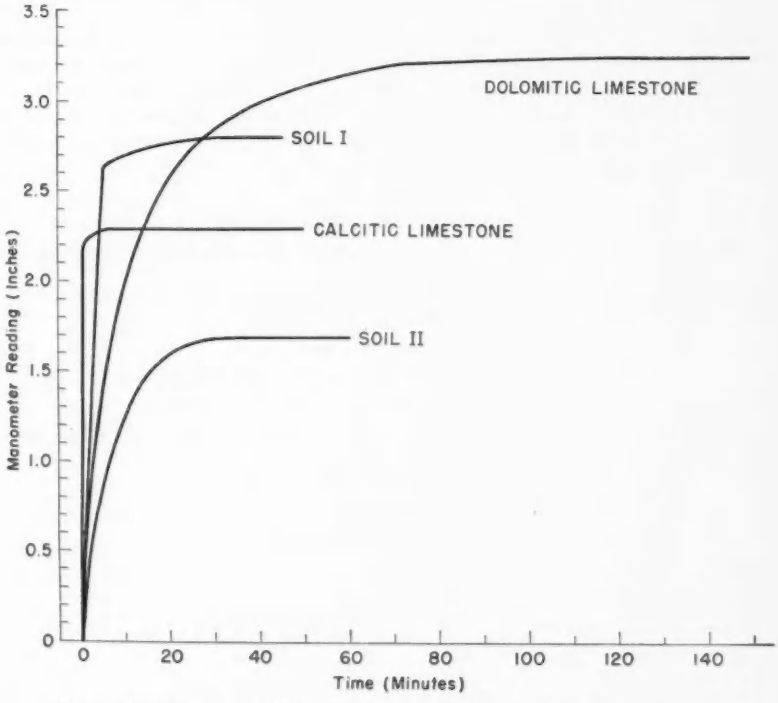



FIGURE 1—Rate of solubility of carbonates in different soils and limestones.

TABLE 1.—ANALYSIS OF STANDARD SAMPLES

| Sample | Per cent carbon dioxide | | |
|---|---|---|---|
| | Rapid method | | Natl. Bur. Standards |
| | Means* | S.D. | Reported |
| Argillaceous limestone No. 1A | 34.4 | ±0.43 | 33.53 |
| Dolomite No. 88 | 47.6 | ±0.74 | 47.25 |
| Fluorspar No. 79 | 0.94 | ±0.07 | 0.95 |

* Based on 5 determinations

Manometer readings are converted to units of carbonate by means of a standard curve, using different amounts of $CaCO_3$ up to one gram. The deficit in volume of the $CaCO_3$ from that of a 5-gram sample of soil is compensated for by addition of a corresponding volume of water. Appreciable fluctuations in temperature must be avoided.

The difference in reaction time required for solution of carbonate in different limestones and soils is illustrated in Figure 1. Results obtained for carbonates in three standard samples agree reasonably well with those reported by the U.S. National Bureau of Standards (Table 1). Where a high degree of precision is not required, the method may be expected to give satisfactory results.

## REFERENCES

1. Martin, A. E., and R. Reeve. A rapid manometric method for determining soil carbonate. Soil Sci. 79:187-197. 1955.
2. Williams, D. E. A rapid manometric method for the determination of carbonate in soils. Soil Sci. Soc. Amer. Proc. 13:127-129. 1948.

—S. I. M. SKINNER,
—R. L. HALSTEAD,
Canada Department of Agriculture,
Ottawa, Canada

May 16, 1958